Chapter IV
Results and Discussion

4.1 Effect of the modifying agent concentration on whiteness property

To measure the effect of the modifying agent on bleaching performance, modified bleached fabric obtained from single-bath treatment was subjected to whiteness index measurement. The results are presented in Table 4-1 and Figure 4.1.

Table 4-1 Whiteness index on modified bleached cotton fabric at various modifying concentrations

Concentrations of Modifying agent	Whiteness Index
Scoured Fabric	39.07
Conventional Bleach	64.375
10 g/l Modifier	64.06
20 g/l Modifier	62.048
30 g/l Modifier	58.811
40 g/l Modifier	56.301
50 g/l Modifier	50.516

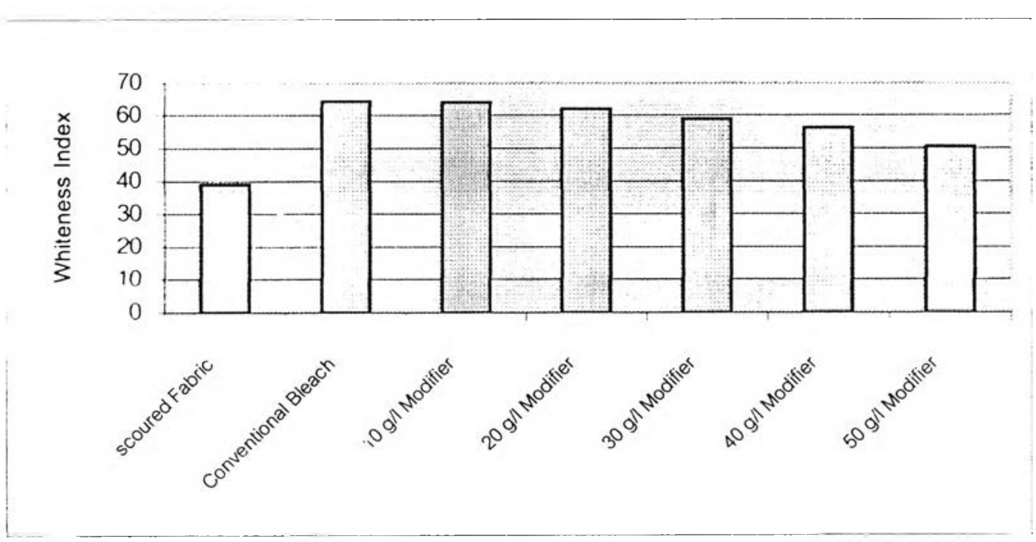


Figure 4.1 Whiteness index chart of modified bleached cotton fabric

As can be seen, conventional bleached fabric exhibited the highest value of whiteness index. The whiteness index of conventional bleached fabric is found to be 64.375%. In the presence of modifying agent, the white appearance of bleached fabrics tended to gradually decrease with an increase in concentration of MAPTAC. It was because residual solution of modifying agent that exhibited pale yellowish color of poly(MAPTAC) also consumed H_2O_2 during consequent bleaching, reducing the bleaching effect on whiteness. However, a slight decrease in whiteness index is observed at the highest concentration of MAPTAC applied (50 g/L). It could be concluded that the addition of modifying agent to bleaching process did not greatly affect the performance of bleaching agent.

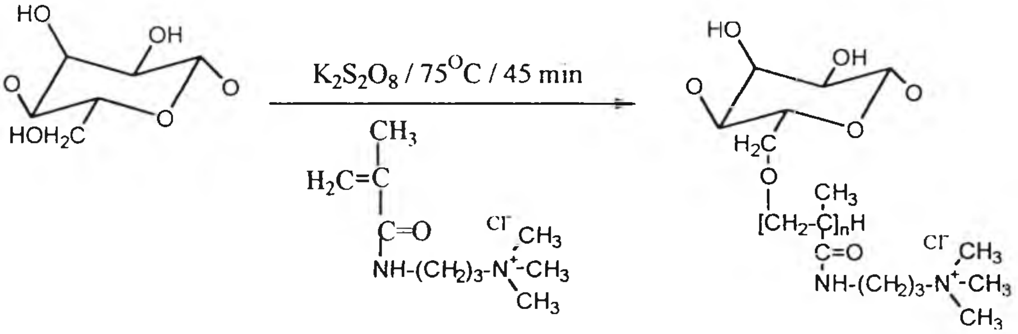
4.2 Total nitrogen content determination

Total nitrogen content of MAPTAC treated cotton was measured in order to evaluate the extent of MAPTAC fixation and the results of total nitrogen content are shown in Table 4-2. The total nitrogen content of MAPTAC treated cotton before adding H_2O_2/NaOH is shown in column 2 while the total nitrogen content of MAPTAC cotton after treating with H_2O_2/NaOH is given in column 3. It can be seen that there was insignificant difference among total nitrogen content values when increasing MAPTAC concentration. The build-up of positive charges on fiber surface was likely to be the main influence causing no further adsorption of the modifying agent. It was thought that once NaOH being added, absorption of cationic MAPTAC should increase further due to the generation of cellulosate anions.

Table 4-2 Total nitrogen content of MAPTAC cotton before and after H_2O_2/NaOH

MAPTAC Concentrations (g/l)	Total Nitrogen Content	
	Before adding H_2O_2/NaOH	After adding H_2O_2/NaOH
10	0.205	0.159
20	0.218	0.193
30	0.204	0.177
40	0.223	0.195
50	0.353	0.312

The total nitrogen content of modified fabric after adding H_2O_2/NaOH increases with an increase in the concentration of MAPTAC. Compared to the corresponding value obtained from modified fabric before H_2O_2/NaOH addition, however, the former value was found to be lower. It was probable that some of absorbed MAPTAC was subjected to alkaline hydrolysis during bleaching, leading to the reduction in the total nitrogen content. In addition, the bleaching condition was also powerful enough to remove unfixed homopolymer and unreacted MAPTAC. Hence, the presence of total nitrogen content indicated the amount of the quaternary ammonium groups attached to the cellulose chain. The increase in total nitrogen content implies the presence of higher amount of anionic dye sites that should mean higher capability of dye uptake. The previous reports suggested that vinyl monomers could be grafted onto cellulose using redox initiators. Therefore it was assumed that the fixation of MAPTAC, one type of vinyl monomers, was also achieved via graft polymerization using $K_2S_2O_8$ as a redox initiator. The function of $K_2S_2O_8$ was to oxidize cellulose hydroxyl groups, thus producing hydroxy free radicals, and then initiating graft polymerization. The graft polymerization reaction of MAPTAC onto cellulose (as already seen in scheme 2.20) may be represented as follows:



From these results, it may be said that bleaching performance obtained from this system such as whiteness, absorbency and removal of mote could meet the bleaching standard required. In addition, cationic groups were also concurrently incorporated into cellulose backbone during bleaching process.

4.3 Effect of increasing concentrations of $K_2S_2O_8$ on dye uptake and dye fixation

Concentrations of $K_2S_2O_8$ were varied from 2 to 10% based on the amount of the modifying agent. Dyeing of modified cotton fabric was then conducted with 2% owf Procion Crimson CX-B at 80^0C for 40 min in the presence of 10 g/L Na_2CO_3. The dye exhaustion and color yield values of resulting dyed fabrics are shown in Table 4-3, Figure 4.2, and Figure 4.3, respectively.

Table 4-3 Color yield and % dye exhaustion of modified fabrics at various concentrations of $K_2S_2O_8$ and liquor ratios

Concentrations of Potassium Persulfate	K/S			% Exhaustion		
	L : R			L : R		
(% based on 20 g/l modifying agent)	1:10	1:20	1:30	1:10	1:20	1:30
2	3.266	3.419	3.095	32.18	37.61	32.92
4	6.078	9.214	8.375	50.03	63.35	54.17
8	12.423	8.022	7.06	77.32	52.66	49.79
10	15.509	8.531	8.807	82.56	54.81	53.24

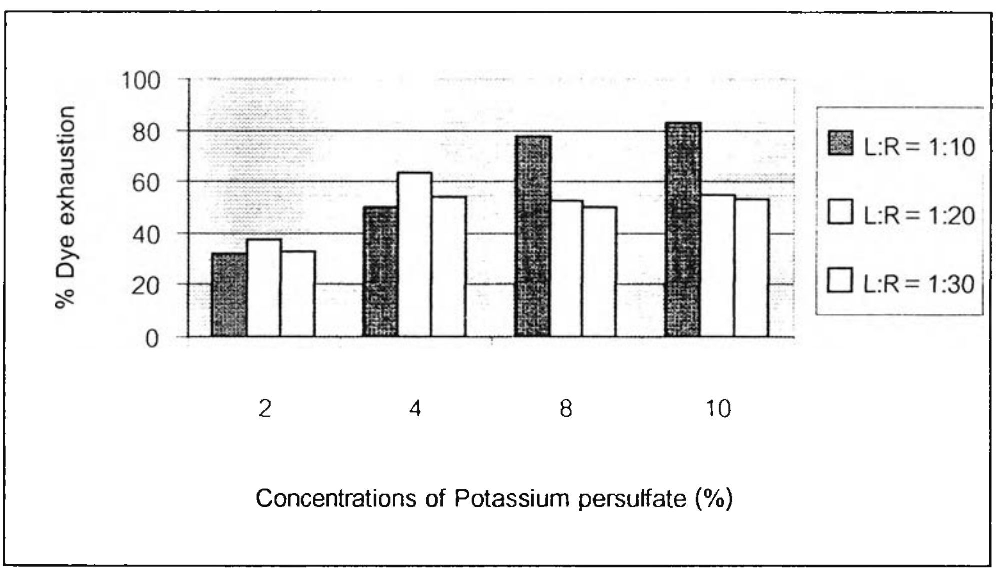


Figure 4.2 Dependence of % dye exhaustion on concentrations of $K_2S_2O_8$ and liquor ratios

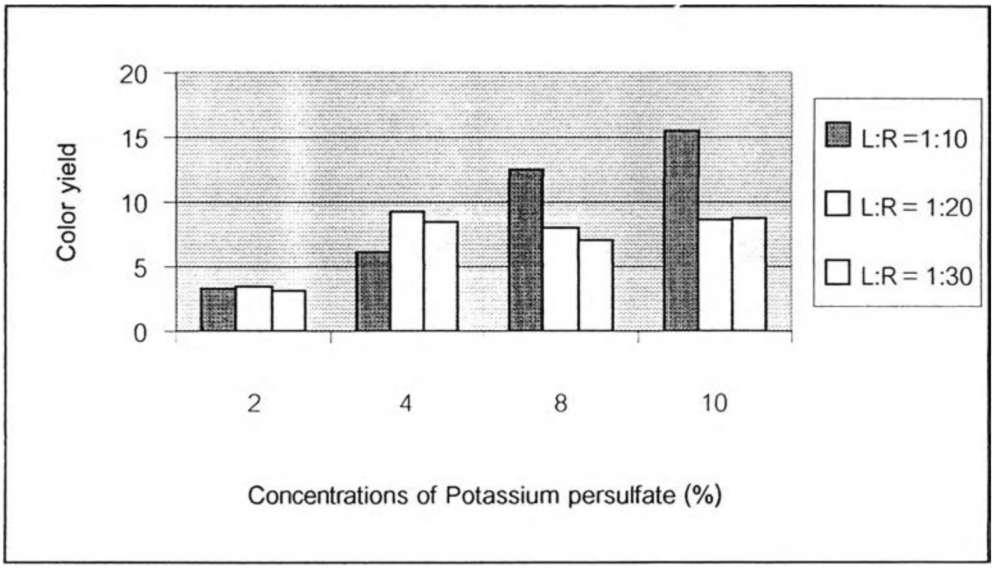


Figure 4.3 Dependence of color yield on concentrations of $K_2S_2O_8$ and liquor ratios

The color strength and % dye exhaustion as indicated in Table 4-3 show an increasing trend with an increase in $K_2S_2O_8$ concentration. The higher $K_2S_2O_8$ concentration produced higher amount of free radicals that, in the similar manner, then generated the radical sites on the fiber. As a result, the graft yield that indicated the amount of dye sites introduced into the fiber was increased with an increase in $K_2S_2O_8$ concentration.

4.4 Effect of liquor ratio on dye uptake and dye fixation

The liquor to goods ratio (L:R) was varied from 1:10, 1:20, and 1:30, and the concentrations of the modifying agent and $K_2S_2O_8$ were fixed at 20 g/l and 4% based on the concentration of modifying agent, respectively. The treatment was carried out at temperature of 75^{0}C for 45 min. Then the modified cotton fabrics were dyed in a solution of 2% owf Procion Crimson CX-B at 80^{0}C for 40 min. in the presence of 10 g/l Na_2CO_3.

The results are already presented in Table 4-3, Figure 4.2, and Figure 4.3, respectively. From the results, the L:R of 1:10 gives the maximum dye uptake and % dye fixation values. However, further increase in liquor ratio tended to suggest that the percent dye uptake and color yield gradually decreased. Higher liquor ratios resulted in decreased chance of the modifying agent to attack the fiber surface. Nevertheless, it could assure that the fabric sample submerged under water for the whole course of treatment process, reducing uneven fixation. The liquor ratio of 1:20 was, therefore, chosen for further experiment in order to balance between those two results.

4.5 Effect of temperature on dye uptake and dye fixation

In order to study the effect of temperature on the dye uptake and dye fixation, the fabrics were treated with 20 g/L modifying agent and $K_2S_2O_8$ 4% of modifying agent at various temperatures ranged from 60 to 90^0 C for 45 min. and then dyed in a solution of 2% owf Procion Crimson CX-B at 80^0 C for 40 min. in the presence of 10 g/l Na_2CO_3. The results were shown in Table 4-4 and in Figure 4.4-4.5, respectively.

Table 4-4 Color strength and % dye exhaustion of modified fabrics at various temperature

Temperature (°C)	K/S	% Exhaustion
60	4.003	37.63
75	6.381	53.62
80	5.144	43.27
90	5.228	42.92

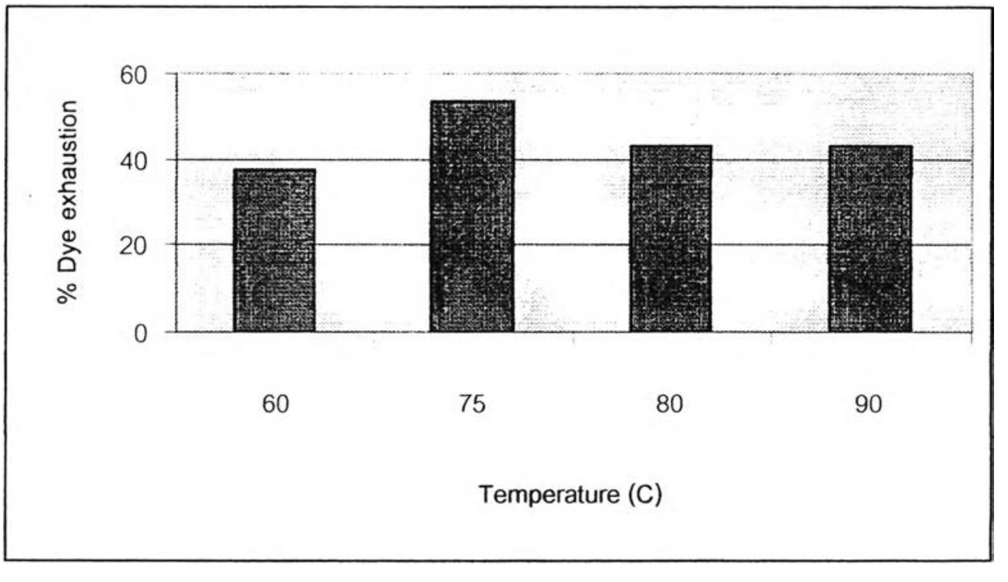


Figure 4.4 Dependence of dye uptake on the temperature

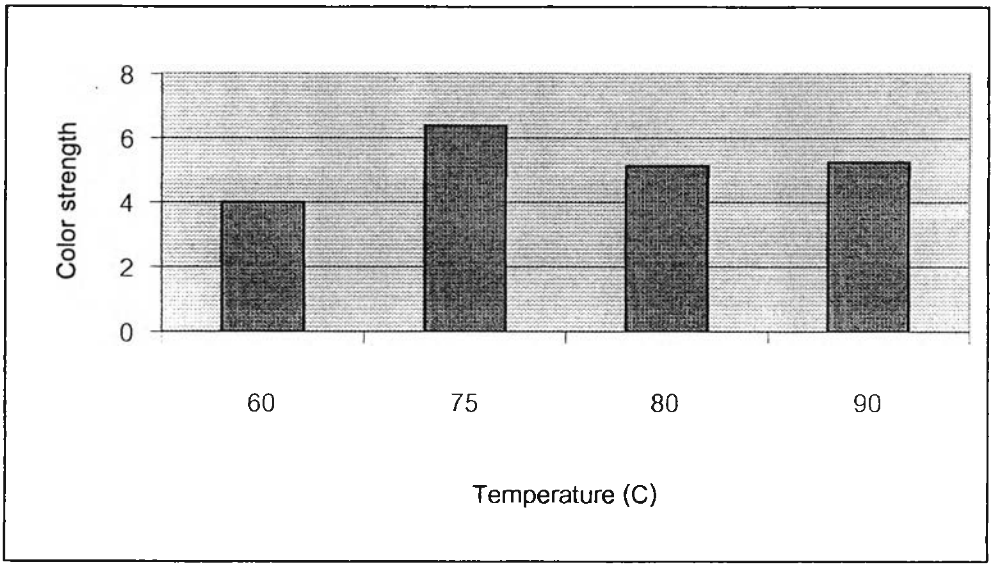


Figure 4.5 Dependence of color strength on the temperature

It can be seen that the percentage of dye exhaustion and color strength of modified fabrics increased when treatment temperature increased from $60^{0}C$ to $75^{o}C$. Further increase in treatment temperature resulted in the dwelling-off of dye uptake as well as color strength. At the temperature above $75^{o}C$, it was probable that excess free radicals produced underwent termination reaction of polymer chain growth, hence lowering graft yield. As a result, the dyeability of modified fabric was decreased. Therefore, in following experiments, all treatments were conducted at the temperature of $75^{o}C$.

4.6 Effect of increasing concentration of modifying agent on dye uptake and dye fixation

The dyeing of modified cotton fabric in the absence of salt was investigated. Cotton fabrics modified with various concentrations of MAPTAC were dyed with 2% owf Procion Crimson CX-B at $80^{0}C$ for 40 min in the presence of 10 g/L Na_2CO_3. The dye exhaustion and color yield values of obtained dyed fabrics are shown in Table 4-5, Figure 4.6 and Figure 4.7.

Table 4-5 Color yield, % dye exhaustion and % fixation of modified fabrics at various modifying concentrations

Concentrations of modifying agent (g/l)	K/S Before soaping	K/S After soaping	% Exhaustion	% Fixation
Conventional bleach	3.624	2.326	38.24	24.54
2.5 g/l Modifier	4.49	2.921	34.24	22.28
5.0 g/l Modifier	4.781	2.813	35.5	20.89
7.5 g/l Modifier	4.396	2.708	38.03	23.43
10 g/l Modifier	4.347	2.912	32.56	21.81
15 g/l Modifier	7.622	5.881	49.79	38.42
20 g/l Modifier	8.393	7.05	49.79	41.82
30 g/l Modifier	9.14	8.017	52.31	45.88
40 g/l Modifier	10.327	9.479	60.08	55.15
50 g/l Modifier	11.416	10.727	78.36	73.63

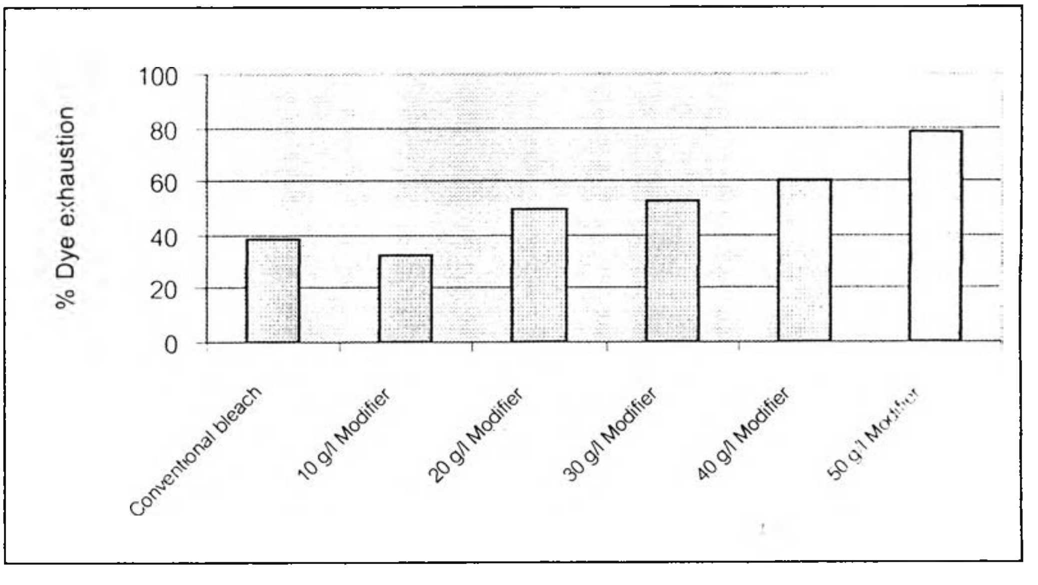


Figure 4.6 Dependence of Dye Uptake on the Concentrations of MAPTAC

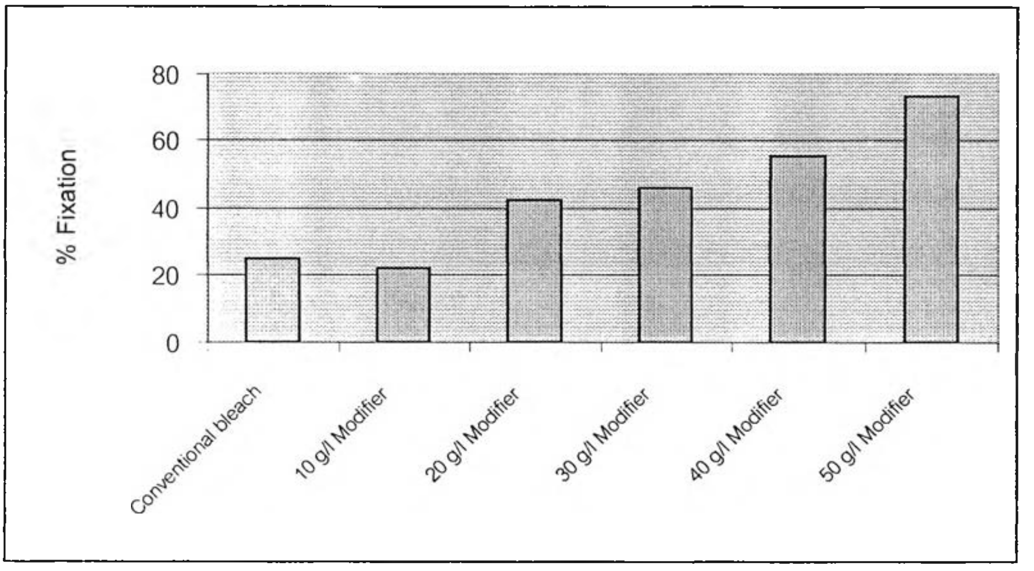


Figure 4.7 Dependence of % Dye fixation on the Concentration of MAPTAC

The result obtained from the control cotton fabric (conventional bleach) demonstrates that the percent dye exhaustion and color strength were quite low due to the repulsive interaction between anionic dye and negatively charged fiber surface. Hence, in order to achieve high dyeability without requirement of salt, it is essential to modify cotton fabric by incorporating cationic sites into cellulose backbone. After being modified, the dye exhaustion and color strength of dyed modified fabric show marked increase with an increase in the concentration of MAPTAC. An enhanced dyeability property of modified cotton fabrics was attributed to the presence of cationic groups that have a large electrostatic affinity with anionic dyes. As a result, the degree of dye exhaustion as well as color strength were closely dependent on the extent of MAPTAC fixation. As can be seen, an increase in MAPTAC concentration from 30 g/L to 50 g/L brings about little change in the extent of MAPTAC fixation, resulting in slight change in color yield. Probably, the build-up of cationic charges acted as a charge barrier to prevent further absorption of MAPTAC inside the fiber. In following experiments up to 40 g/L MAPTAC was employed since, in practice, higher concentration is not preferable due to the cost of modifying agent itself and possible yellowing of bleached fabrics.

4.7 Effect of different dye types on dye uptake and color yield

Two types of dyes, low substantivity (Procion Red) and high substantivity (Modercion Navy Blue) were chosen to study the effect of dye types on dye uptake and color yield. The results are presented in Table 4-6.

Table 4-6 Color yield, % dye exhaustion and % fixation of modified dyed fabrics at different dye types

Concentrations of modifying agent (g/l)	K/S				% Exhaustion		% Fixation	
	Before soaping		After soaping					
	Blue	Red	Blue	Red	Blue	Red	Blue	Red
Conventional bleach	6.495	3.624	5.254	2.326	54.74	38.24	44.28	24.54
2.5 g/l Modifier	6.4	4.49	5.361	2.921	61.23	34.24	51.29	22.28
5.0 g/l Modifier	6.681	4.781	5.416	2.813	62.63	35.5	50.77	20.89
7.5 g/l Modifier	6.56	4.396	5.431	2.708	61.4	38.03	50.83	23.43
10 g/l Modifier	6.342	4.347	5.479	2.912	61.93	32.56	53.5	21.81
15 g/l Modifier	8.541	7.622	7.82	5.881	79.12	49.79	72.44	38.42
20 g/l Modifier	8.759	8.393	8.348	7.05	82.63	49.79	78.75	41.82
30 g/l Modifier	8.794	9.14	8.288	8.017	87.02	52.31	82.01	45.88
40 g/l Modifier	9.165	10.327	8.645	9.479	90.35	60.08	85.22	55.15
50 g/l Modifier	8.535	11.416	8.335	10.727	92.28	78.36	90.12	73.63

Compared with Procion Red, Modercion Navy Blue exhibited higher exhaustion on control and on modified fabric due to its high substantive characteristic towards cotton fiber. Moreover, for the modified fabrics, the very high exhaustion (over 90%) could be achieved in the case of fabric being treated with 50 g/l modifying agent. Therefore, it is possible to achieve complete exhaustion (clear dye bath solution) if the high substantive dyes are selected. Such dyeing results are hardly obtainable in the case of conventional dyeing (dyeing with salt addition).

4.8 Effect of increasing dye concentration on dye uptake and color strength

Cotton fabrics modified with various concentrations of MAPTAC in bleaching process were dyed with 1, 2, 3, and 4% owf Procion Crimson CX-B and Modercion Navy Blue at 80^{0}C for 40 min in the presence of 10 g/L Na_2CO_3. The dye exhaustion values and color strength of resulting dyed fabrics are shown in Table 4-7

Table 4-7 Effect of Increasing Dye Concentration on Dyeing Properties of Modified Fabric

Concentrations of MAPTAC (g/l)		Dye concentrations							
		1% owf		2% owf		3% owf		4% owf	
		K/S	%E	K/S	%E	K/S	%E	K/S	%E
Control	Blue	3.089	75	5.254	54.74	6.126	52.81	7.602	47.33
	Red	1.717	55.68	2.326	38.24	3.254	32.6	3.667	32.45
10	Blue	2.972	68.91	5.479	61.93	7.038	51.06	8.424	47.91
	Red	1.792	62.22	2.912	32.56	3.533	35.67	4.601	31.29
20	Blue	5.024	94.55	8.348	82.63	9.72	70.54	11.319	59.55
	Red	5.714	84.09	7.05	49.79	7.442	50.58	7.602	34.25
30	Blue	4.989	97.44	8.288	87.02	10.267	74.03	12.02	64.5
	Red	8.077	82.1	8.017	52.31	10.252	38.6	9.586	44.82
40	Blue	4.572	98.4	8.645	90.35	10.815	82.27	14.09	73.23
	Red	7.046	87.78	9.479	60.08	10.905	50.29	12.517	46.51
50	Blue	5.166	98.4	8.335	92.28	11.004	78.78	15.21	74.2
	Red	8.085	92.05	10.727	78.36	11.104	49.71	11.587	52.85

In all cases of MAPTAC concentrations, trends of percent dye exhaustion is gradually reduced as the concentration of dye increases. Differently, color strength increases with an increase in dye concentration and reached the optimum value, and then further increase in dye concentration resulted in little decrease in color strength. It is believed that dye exhaustion was controlled by ionic-ionic interaction, hence the amount of absorbed dye was exactly dependent on the amount of cationic sites inside the fiber. Once the cationic sites were fully occupied, there were no further dye exhaustion take place. This type of dye absorption was suited well with Langmuir absorption isotherm. These results obtained were found to contradict those obtained from conventional reactive dyeing where increased dye concentration always results in a gradual increase in color strength. Therefore, dyeing of cationic cotton may offer an advantage in terms of reproducibility when compared to conventional dyeing since depth of color shade is not so sensitive to a small variation of changes in dyebath concentration. Between 30 g/L and 40 g/L modifying agent, it seemed that there was little difference between the extent of color strength, indicating the leveling-off of the degree of modifier fixation.

The build-up of positive charge on fiber surface was likely to be the main influence causing no further absorption of the modifying agent above the concentration of 30 g/L. This phenomenon was found similarly with the dyeing of cellulose with cationic reactive dye.

4.9 Microscopic analysis of cross-section of dyed yarn

Microscopic analysis of the cross-section of MAPTAC treated yarns dyed with 2% owf Procion Crimson CX-B is shown in Figure 4.8. The distribution of dye on treated yarn indirectly indicated the distribution of modifying agent across the treated yarn. Even distribution of modifying agent across the treated yarn is required in order to obtain good dyeing properties including even dyeing and light fastness.

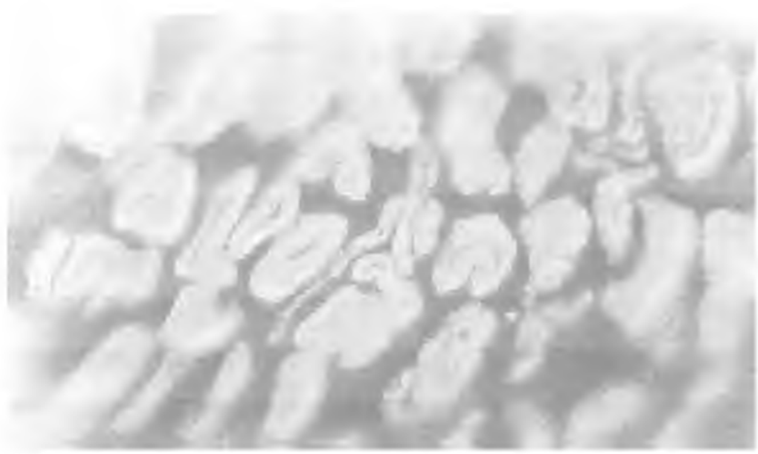


Figure 4.8 Optical micrograph of MAPTAC treated yarn dyed with 2% owf Procion Crimson CX-B

From the figure, individual fibers on the yarn surface and in the inner of yarn exhibited even distribution of dyes, indicating the good migration property of modifying agent that was attributed to its low molecular weight.

Furthermore, since this compound carries a cationic group, the substantivity towards cotton fiber should be high enough to force the modifying agent to diffuse into the inner of the fiber. Consequently, graft polymerization of MAPTAC onto cellulose using $K_2S_2O_8$ initiator produced high molecular weight polymer that could be covalently fixed evenly across cotton yarn. This is the distinct advantage of low molecular weight compound over high molecular weight agent that posseses high substantivity towards cotton but poor migration. As a result, such compound tends to stay on yarn surface, leading to ring dyeing and poor light fastness.

4.10 Evaluation of color fastness to light

This study was to investigate the influence of the presence of caionic groups on the light fastness property of dyed cationic fabric. Fastness to light of modified cotton fabrics dyed with 2% owf Procion Crimson CX-B and Modercion Navy Blue at $80^{0}C$ for 40 min in the presence of 10 g/L Na_2CO_3 and then soaped in a solution containing 5 g/l NaOH and 5 g/l nonionic surfactant at the boil for 20 min. (liquor ratio 1:50) was conducted using Xenon Weather Meter (as seen in Figure 3.7), Model X75 (Suga Test Instruments Co., LTD, Japan). The results are shown in Table 4-8

Table 4-8 Light fastness of dyed cotton fabrics modified with various concentrations of modifying agent

Concentrations of modifying agent		Light Fastness Rating
Control	Blue	2-3
	Red	2-3
10 g/l	Blue	1-2
	Red	2-3
20 g/l	Blue	1
	Red	1-2
30 g/l	Blue	1
	Red	1-2
40 g/l	Blue	1
	Red	1-2
50 g/l	Blue	1
	Red	1-2

Table 4-8 shows that, regardless to dye types, light fastness rating of dyed fabrics decreased with an increase in the amount of the modifying agent applied. This indicated that the presence of cationic groups caused the reduction in fastness to light. Partly, the cationic group is known as photocatalyst that might accelerate the rate of dye decomposition. Another possibility was that the cationic modifying agent tended to locate on the yarn surface, resulting in consequent surface dyeing. Therefore, the surface dye was prone to photo-degradation when compared to conventional dyeing. It is recommended that the cationic groups should be removed at the end of dyeing process in order to improve fastness to light.

4.11 Dyeing of unmodified cotton fabrics

Dyeings of unmodified cotton fabrics using different concentrations of commercial Procion Crimson CX-B and Modercion Navy Blue (1%, 2%, 3%, and 4% owf) were conducted in similar manner to the dyeing of modified fabrics except various amount of electrolyte (NaCl 20,30,40 g/l) were added into the dye solution at the temperature of 50^{0} C for 10 min. Dyeing properties of resulting fabrics are shown in Table 4-9 and Table 4-10, respectively.

Table 4-9 Color yield, and % dye exhaustion of unmodified fabrics dyed with various concentrations of electrolyte

Concentrations of electrolyte (g/l)		Dye concentrations							
		1% owf		2% owf		3% owf		4% owf	
		K/S	%E	K/S	%E	K/S	%E	K/S	%E
20	Blue	4.346	89.42	8.186	83.86	11.004	77.4	12.68	73.12
	Red	4.446	77.84	6.563	52.73	9.316	45.32	11.473	49.26
30	Blue	4.979	91.99	8.242	88.6	11.948	84.02	13.686	78.08
	Red	5.571	85.23	9.058	71.85	11.606	59.8	12.832	59.83
40	Blue	4.782	94.23	8.594	92.98	12.225	86.02	15.003	81.47
	Red	6.07	87.22	9.995	72.26	12.907	63.89	14.475	63.64

Table 4-10 Light fastness of unmodified cotton fabrics dyed with various concentrations of dyes

Concentrations of electrolyte	Light Fastness							
	1% owf		2% owf		3% owf		4% owf	
	Blue	Red	Blue	Red	Blue	Red	Blue	Red
20 g/l	2-3	3-4	2-3	3-4	2-3	3-4	2-3	3-4
30 g/l	2-3	3-4	3-4	3-4	3-4	3-4	3-4	3-4
40 g/l	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4

As can be seen from Table 4-10, light fastness of dyed unmodified cotton fabrics increases with an increase in concentration of salt. Red dye exhibits the higher light fastness values than the blue one. It can be concluded that the presence of salt promotes the deeper penetration of dye molecules to the inner of fiber yarn, hence avoiding the direct exposure to light. As a result, light fastness of conventional dyeing is still greater compared to cationic cotton fiber.