Some Studies on Dyes for Coloration of Paper

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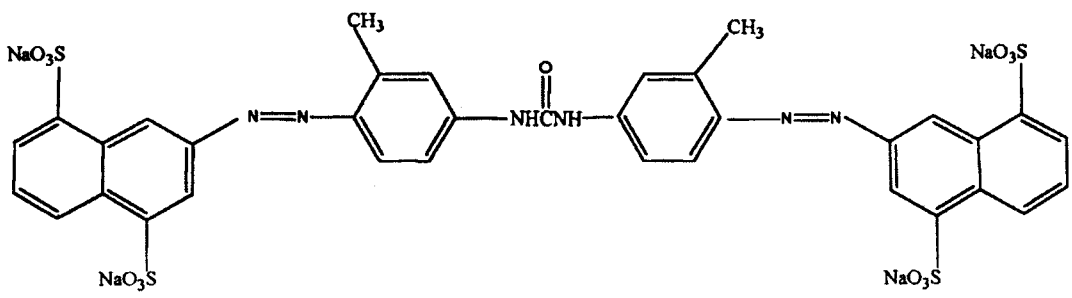
The study covers the coloration of cellulose fibres with four direct dyes. The prepared paper samples were of yellow, red, violet and orange colors in different shades using 0.5% dye (related to the absolutely dry fibrous materials). Also a cationic agent was used to improve the wet fastness of the dyes under investigation the coloration was evaluated by CIELab coordinates. The obtained results indicated that the mechanical properties of paper sheets can be enhanced by increment of dye concentration, while an inhibition took place by: i-rising dyeing temperature, ii- increment of agent concentration. The relation between dye structure and mechanical properties was not clear.

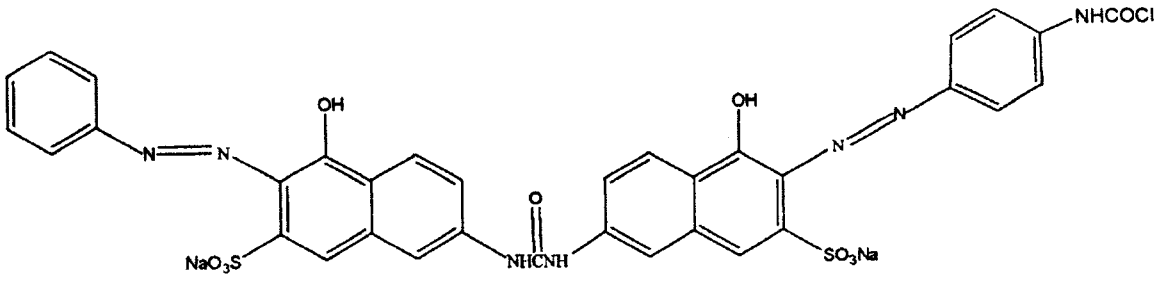
INTRODUCTION

The production of colored paper favors the utilization of cellulose of lower whiteness, high yield pulp, waste paper, etc. (1& 2). On the other hand, by improving its appearance and quality we benefit of larger variety of paper to be used for writing, printing and publishing. It is of great importance to produce paper of bright colors which do not fade under the effect of light and temperature, a quality determined both by the structure of the dyes and the dyeing technology.

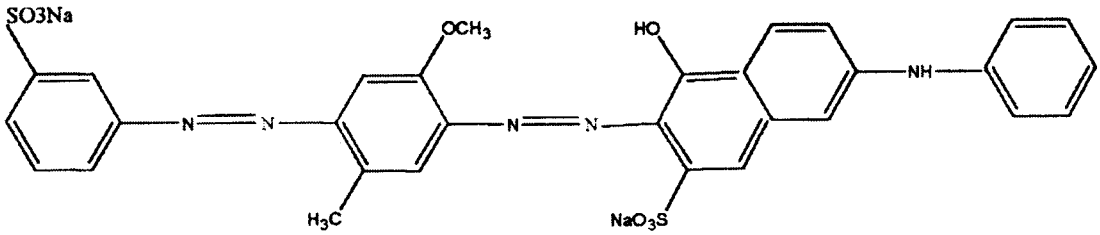
As paper production greatly increased, so the market for specialty dyes was realized, and in 1981 worldwide consumption of dyes in paper was estimated by Martin (3) at 3700 tonnes (in powder form). Direct dyes now a count for about 60 % of the paper market (4). These dyes exhibit both good substantively and affinity (5), and also a' great reduction in the amount of dye present in the back water (3&6). The azo dye which is one type of direct dye is the largest and most important group (7). They furnish yellow red coloring. It is typical to have low photo and thermal stability .The later fact is due to trans-cis isomerization or destruction of the dye chromophoric system during photo- and thermal treatment, which is a part of drying process. The use of direct dyes which are cheaper and easily for



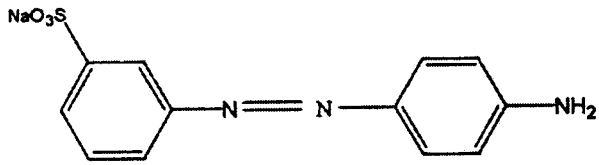
Direct Yellow 50 (C.I. 29025)



Direct red dye 23 (C.I. 29160)

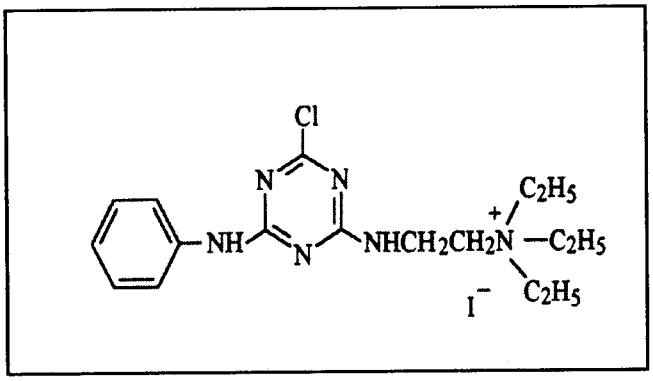


Violet direct dye 31 (C.I. 27880)



Direct Orange

dyeing cellulose has a defect. The defect is of lower wet fastness.



The present work was aimed to use a cationic agent to improve the wet fastness of the dyes under investigation and also to study the effect of dye cationic agent structure on the paper properties.

EXPERIMENTAL

- **Materials**

- Bleached sulfate wood pulp was beated to 40°SR in a valley beater.

- Direct dyes were of commercial source and having

Table 1 : Some Properties of dyes under investigation

Dye No.	Dye Name	Color Index (C.I.)	λ_{max} (nm)
I	Direct Yellow 50	29025	395
II	Direct Red 23	29160	497
III	Direct Violet 31	27880	542
IV	Direct Orange		398

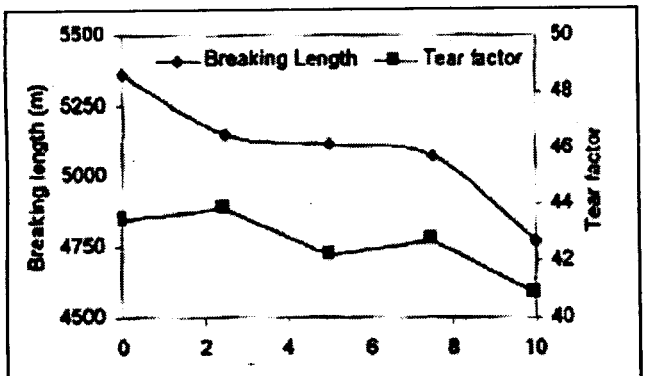


Fig.1: Effect of cationic agent on the mechanical properties of un-dyed paper sheets

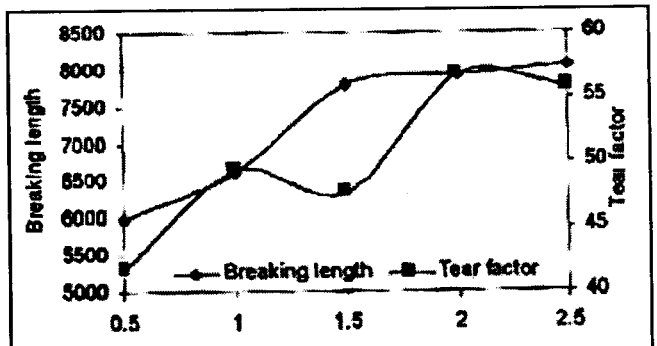


Fig.3: Effect of dye concentration on mechanical properties of treated paper sheets dyed with yellow dye.

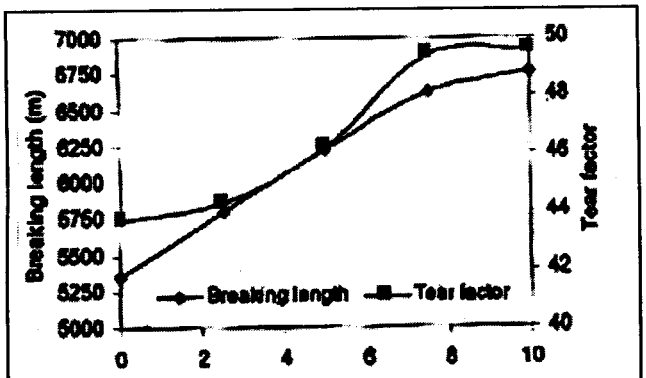


Fig.2: Effect of cationic agent on the concentration on mechanical properties of dyed paper

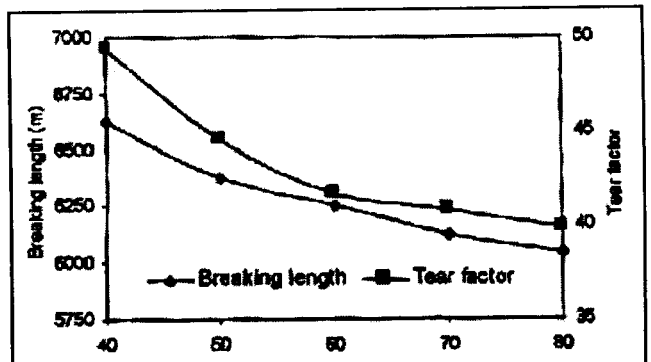


Fig.4: Effect of dyeing temperature on mechanical properties of treated paper sheets dyed with yellow

Table 2 : Effect of dye structure on mechanical properties of treated and untreated dyed paper.

dye	Untreated paper		Treated paper	
	Breaking length (m)	Tear factor	Breaking length (m)	Tear factor
Yellow	5385	43.7	6627	49. 4
Red	4879	51.6	5515	48. 6
Violet	5277	55.0	5110	60. 8
Orange	5542	42.0	5378	51. 8

the following structure.

Cationic agent was prepared according to the method described by Y. Youssef (8). Its structure was as follows

- **Methods**

- Paper making; hand sheets of basis weight of 68g/m^2 were prepared according to Swedish Standard Methods (SCA). The mechanical properties

Table 3: Effect of cationic agent concentration (treatment temperature 40°C, L.R. 1:40 sade 1%)

Agent concentration %	E%	Before dyeing				After dyeing			
		K/S	L*	a*	b*	K/S	L*	a*	b*
0	23.5	0.1864	45.1	-14.34	-18.38	0.238	46.26	-14.23	-20.13
2.5	32.5	0.1853	44.59	-13.87	-14.11	0.22	45.72	14.13	-17.68
5	52.5	0.228	44.81	-12.02	-14.96	0.272	44. 68	-12.64	-11.94
7.5	61.5	0.228	43.13	-10.95	-15.92	0.296	44.12	-11.41	-11.04
10	64.5	0.365	43.6	-10.47	-13.55	0.406	43.92	-10.45	-9.81

Table 4: Effect of dye concentration (cationic agent conc. 7.5%, L.R. 1:40)

Shade %	E%	Before dyeing				After dyeing at 140°C for 2 hours			
		K/S	L*	a*	b*	K/S	L*	a*	b*
0.5	64.5	0.256	44.0	-8.11	-17.03	0.228	44.78	-8.08	-18.11
1.0	61.5	0.288	43.13	-10.95	-15.92	0.269	44.12	-11.41	-11.04
1.5	59.5	0.626	42.28	-13.45	-14.11	0.273	44.09	-12.44	-16.02
2	55.0	0.714	42.12	-11.yy	-10.94	0.359	42.46	-11.75	-12.06
2.5	52.5	0.807	40.11	-10.11	−7.84	0.408	40.09	-9.99	-10.03

Table 5 : Effect of dyeing temperature (L.R. 1:40, shade 1%, agent conc. 7.5%)

Dyeing temp. °C	E%	Before dyeing				After dyeing			
		K/S	L*	a*	b*	K/S	L*	a*	b*
40	61.5	0.288	43.13	-10.95	-15.92	0.676	44.12 -	-11.41	-11.04
50	60.0	0.348	44.24	-13.47	-20.94	0.278	43.87	-12.72	-18.96
60	59.5	0.319	43.52	-13.63	-20.09	0.293	43.63	-13.50	-19.33
70	60.5	0.290	42.25	-13.78	-19.69	0.282	42.36	-14.27	-19.69
80	61.0	0.261	41.03	-14.01	-19.66	0.254	40 .93	-14.11	-19.56

Table 6: Effect of dye structure on untreated paper sheets (L.R I :40, treatment temp. 40°C, shade1%, agent concentration. 7.5%) .

Dye name	E%	Before aging				After aging at 140°C for 2 hours			
		K/S	L*	a*	b*	K/S	L*	a*	b*
Yellow	23.5	0.1864	45.1	-14.34	-18.38	0.238	46.26	-14.23 .	-20.13
Red	46.5	2.62	36.78	7.66	-33.49	2.52	36.49	7.2	-33.5
Violet	31.0	1.067	35.77	-1.09	-59.88	1.096	35.59	-1.19	-59.13
Orange	27.0	0.0285	45.11	-8.92	-25.24	0.03	45.0	-9.2	-25.46

Table 7: Effect of dye structure on treated paper sheets (L.R I :40, temp. of treatment, 40°C, shade 1%, agent concentration 7.5%)

Dye name	E%	Before aging				After aging at 140°C for 2hours			
		K/S	L*	a*	b*	K/S	L*	a*	b*
Yellow	61.5	0.288	43.13	-10.95	-15.92	0.269	44.12	-11.41	-11.04
· Red	94.0	3.26	34.59	6.13	-32.43	3.23	34.95	5.82	-32.14
Violet	96.5	3.24	30.93	1.34	-56.61	2.39	31.10	-0.01	-54.42
Orange	69.5	0.348	45.84	-4.95	-21.58	0.356	41.75	-5.13	-18.85

(breaking length and tear factor) were determined according to Standard Methods.

- Thermal treatment; treated and untreated dyed paper sheets were aged at 140°C for 2 hours.

- Color measurements; for quantitative and qualitative characterization of the color in the color range according CIELab space, is determined by axes of plane. These are axes a*, b* and L*. Hunter lab. Apparatus was used for measuring. K/S was measured by Perkin Elmer spectrophotometer.

RESULTS AND DISCUSSION

At first, the effect of cationic agent on the mechanical properties of paper sheets (un-dyed and dyed with yellow dye at 40°C, L.R 1:40 and shade 1%) was studied. The .w- obtained results were showed in Figs. 1&2.

- **Effect of cationic agent concentration**

It is clear from results showed in Fig.1, that the effect of cationic agent concentration on both breaking length and tear factor of dyed paper sheets increases with increment of agent concentration. This can be clear if the physical and chemical reaction of the agent with the paper sheets will be discussed. The cationic agent has an active chlorine atom. This Cl can react with OH of cellulose leaving the other end of the agent [$^{+}(C_2H_5)_3I^{-}$] to react with the direct dyes

under investigation. As clear from the above Fig., increasing the agent concentration decreases both the breaking length and tear factors. This can be attributed to the inhibition of the inter fibre bonding caused by the agent, which reacts only by one end with the hydroxyl groups of cellulose chain by the positively charged nitrogen.

- **Effect of dye concentration on the paper sheets properties**

It is clear from Fig.3 that both the breaking length and tear factor increased with the increment of dye concentration. This may due to: i- the reacted dye reacted directly with cellulose and protecting it, ii- direct dye reacts with the cationic agent and also plays the same role as those reacting directly with cellulose. Therefore, increasing dye concentration enhances both breaking length and tear factor.

- **Effect of dyeing temperature**

Results showed in Fig. 4 show that the breaking length and tear factor decreased with dyeing temperature increment. This can be due to at higher dyeing temperature the bond founded between cellulose and both dye or the agent easily hydrolyzed at temperature higher than 40°C. As mentioned above both dye and agent causes increment on breaking length and tear factor. Hydrolyzing them decrease this enhancement showed by treated paper sheets.

- **Effect of dye structure**

From results showed in Fig.3, it is clear that, as mentioned before, the increase in dye concentration caused an increment in both breaking length and tear factor. This can be attributed to the hydrogen bond formed between the direct dye used and the cellulose molecule of the paper sheets. When using different direct dyes of different chemical structure for dyeing untreated or treated paper sheets under investigation, the relation between the chemical structure of the used dyes and the mechanical properties of the paper was not clear (c.f table 2).

- **Color analysis for the effect of cationic agent on the color of paper sheets**

For determination any change in the color of paper sheets under investigation before or after dyeing, the optimum conditions for using the agent and/ or dyes was determined. At the same time the L*, a* and b* of the colored paper sheets was measured. The dye used in this study was the Yellow one. The obtained results were cite in the following tables (3- 7).

The effect of cationic agent on the color of paper sheets can be discussed as follows: I-Effect on K/ S

It is clear from results in table 7, that E% and K/S increased at higher concentration of the cationic agent used.

2-Effect on L*

As well known L* decreases as the dye shade increases. A result in table 3 reflects these phenomena.

3-Effect on a* and b*

For a*, increasing agent concentration caused a movement of the sample color from green towards red color. For b*, the same thing took place i.e. its movement towards yellow color increased with the increment in the agent concentration.

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