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Synthesis and Application of 2:1 Zinc Complex Dyes and Their Antibacterial Properties

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2:1 Zinc complex monoazo acid dyes have been prepared. Six commercially available Omega Chrome dyes and other three dyes based on 1-amino-2-naphthol-6-sulphonic acid and the couplers 1-naphthol-4-sulphonic acid, 2-naphthol and 2-naphthol-6-sulphonic acid were used in preparing the complexes. All these dyes were analyzed using atomic absorption spectra and thin layer chromotogrphy. The dyeing of wool fabric was carried with these dyes and their antibacterial activity of dyed fabric was assessed. Dyeings using zinc complexed dyes showed prominent antibacterial activity. The performance properties such as wash fastness, fastness to dry cleaning and light fastness were also measured. Intense colour value was obtained for all the dyes synthesized. Very good fastness to washing and dry cleaning has also been observed, where as light fastness of the deyings was of moderate to good degree.

Key Words: Antibacterial dyes, Zinc complexes.

INTRODUCTION

There are a variety of factors like weather conditions, atmospheric pollution, light and biological action contributing to the degradation of textiles. Biological deterioration is caused by microorganisms such as bacteria and fungi. High relative humidity, warm temperatures and source of nutrient are the favourable conditions for the rapid growth of microorganisms. They grow into large colonies or mycelia, which bring about degradation of textiles. The growth leads not only to textile degradation, but has also a variety of serious consequences in the medicinal and health care areas. Natural fibres like wool, cotton and silk retain water readily and provide nutrient to micro-organisms and hence they are more prone to attack while synthetic fibres do not do so. However, some microbes grow in colonies in synthetic fibres also, though in a slower fashion, particularly if some finishing agents support their growth.

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Preventing biological degradation of textiles has been widely done by proper finishing treatments. A number of finishing agents have been developed and used commercially. However, majority of such finishing agents are durable to a few launderings only giving just a temporary resistance against microbes.

In recent years, it has been demonstrated that textile colouration and functional finishing processes can be combined[1-4]. However, application of such one step processes may have serious limitations due to the different treatment conditions required for textile colouration and functional finishing. In an alternative approach, dyes having special functional properties may be developed. This concept has been fully utilized *e.g.* in the design of light fast dyes by incorporating ultraviolet absorber units in the dye molecule[5,6]. In recent years the concept has also been extended to the synthesis of antimicrobial cationic dyes[7].

In this paper, synthesis of zinc complexed dyes having inherent antimicrobial properties has been described. Application of these dyes on textiles for obtaining a more permanent way of microbial protection to textiles, has been investigated.

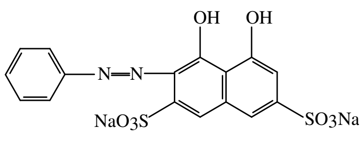
EXPERIMENTAL

The following commercially available Omega Chrome dyes are converted to their 2:1 zinc complexes:

Omega Chrome Fast Blue B (**I**), Omega Chrome Brown EB (**II**), Omega Chrome Bordeaux BR (**III**), Omega Chrome Brown 2R (**IV**), Omega Chrome Yellow K (**V**) and Omega Chrome Black S Supra (**VI**).The structure of these dyes (**I-VI**) are given in Fig. 1. Three other dyes (**VII, VIII** and **IX**) were prepared and converted into 2:1 zinc complexes.

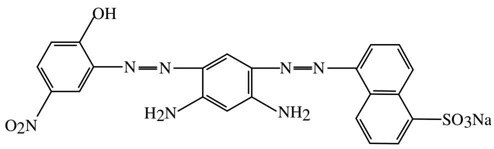
Synthesis of dye VII: A mixture of 6 g (80 % purity, 0.02 mol) of 1-amino-2-naphthol-4-sulphonic acid and 20 mL of water was cooled externally to 0-5°C. Copper sulphate (4 g) was added and hence a solution of 5 N sodium nitrite (4 mL) was added gradually with stirring and reaction was continued for 0.5 h. The solution was transparent and the diazonium salt was obtained as precipitate on addition of 6 mL of HCl. The precipitate was filtered off and washed with dilute HCl.

1-Naphthol-4-sulphonic acid (6.4 g, 69 % purity, 0.2 mol) was dissolved in minimum quantity of water and pH of the solution was adjusted to 8-8.5 using sodium carbonate solution. The diazonium salt prepared earlier was added gradually with constant stirring. The pH of the solution was adjusted to 8 and the reaction was continued at this pH for 4 h. The dye was filtered, dissolved in minimum quantity of water at 60°C and salted out using sodium chloride (15 % w/v), filtered and dried. Yield obtained was 77 %.



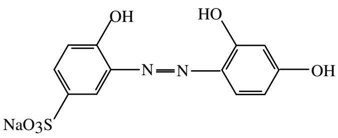
Omega Chrome Fast Blue B

I



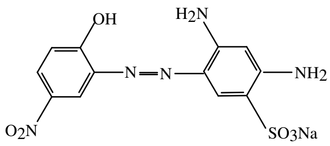
Omega Chrome Brown EB

II



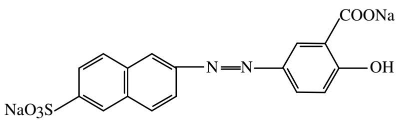
Omega Chrome Bordeaux BR

III



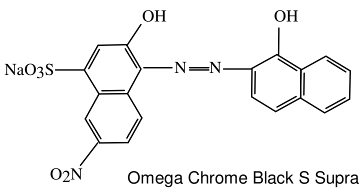
Omega Chrome Brown 2RI

IV



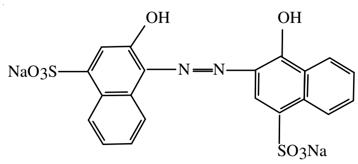
Omega Chrome Yellow K

V



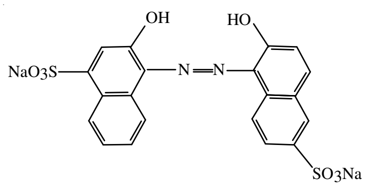
Omega Chrome Black S Supra

VI



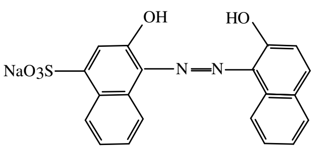
1,2,4 - Acid → NW Acid

VII



1,2,4 - Acid → Schaffer's Acid

VIII



1,2,4-Acid → β-Naphthol

IX

Fig. 1. Structures of Omega Chrome dyes

Synthesis of dyes VIII and IX: They were prepared using a procedure analogous to that described for the preparation of the dye **VII**. 2-Naphthol-6-sulphonic was used as the coupler for the dye **VIII** and 2-naphthol was used as the coupler for the dye **IX**.

Preparation of 2:1 zinc complexes: A mixture of dye (250 mg) and zinc sulphate septa hydrate ($ZnSO_4 \cdot 7H_2O$) (250 mg) was dissolved in 10 mL water and refluxed with stirring for 4 h. The dye was salted out by adding 15 % w/v of sodium chloride at 60°C. The slurry was filtered at 60°C, washed and dried. Yield obtained was 68 % . The dyes synthesized are given in Table-1.

TABLE-1
2:1 ZINC COMPLEX DYES SYNTHESIZED

Dye no.	Dye, Zinc complex of
X	**I**, Omega chrome fast blue B
XI	**II**, Omega chrome brown EB
XII	**III**, Omega chrome bordeaux BR
XIII	**IV**, Omega chrome brown 2 RI
XIV	**V**, Omega chrome yellow K
XV	**VI**, Omega chrome black S supra
XVI	**VII**, 1,2,4-Acid → NW Acid
XVII	**VIII**, 1,2,4-Acid → Schaeffer's acid
XVIII	**IX**, 1,2,4 Acid → β-Naphthol

The atomic absorption spectra of representative zinc complexed dyes are shown in Table-2. The data confirms that the complexes are all of 2:1 type. The atomic absorption spectra were recorded using GBC 932 Plus atomic absorption spectrophotometer.

TABLE-2
ATOMIC ABSORPTION VALUES OF 2:1 ZINC COMPLEXED DYES

Dye no.	Dye	Conc. of dye soln. (ppm)	Conc. of zinc (ppm)
XVI	Zinc Complex of 1,2,4 Acid → NW Acid	10	0.680
XVII	Zinc Complex of 1,2,4 Acid → Schaffer's Acid	10	0.636
XVIII	Zinc Complex of 1,2,4 Acid → β-Naphthol	10	0.810

Thin layer chromatography and visible absorption spectra: Thin layer chromatography was carried out by spotting an aqueous solution of the dye on a thin layer of neutral alumina and eluting using the solvent of composition-butanol:pyridine:water (2:2:1). The colours of the aqueous solution of the dye, the colours observed on TLC plate, the R_f values of the spot and the maximum wavelength of absorption in water are presented in Table-3.

Dyeing with premetallized dyes: The fabric was treated at 40°C for 10 min in a bath set with 2 % ammonium sulphate (pH range is 5 to 6). The dissolved dye was then added and the temperature was raised to boil (for silk 85°C) in 45 min. Dyeing was continued at this temperature for 1 h.

Post dyeing metallization process for wool fabrics: The wool fabric was treated at 40°C for 10 min in a bath set with 2 % acetic acid. The dissolved dye was then added and the temperature was raised to boil in 45 min. Dyeing was continued at this temperature for 0.5 h. The dye bath was then exhausted, whenever needed, by adding more acetic acid. When the dye bath has been exhausted completely, it was cooled to 70°C and 1 % $ZnSO_4 \cdot 7H_2O$ was added. The temperature was raised to boil and this treatment was continued for further 1 h.

Antimicrobial test

Method-I: For evaluating antibacterial activity AATCC Test method 90-1970 Agar Plate method was employed. Plate count agar was melted and taken in two conical flasks. Agar in one flask was inoculated with standard strain of *Staphylococcus aureus* (obtained from NCL, Pune, India). 15 mL of unseeded agar was poured in 100 mm diameter flat-bottomed Petri dish. It was solidified by cooling it for 15 min. Then 15 mL seeded agar was poured in it. After the second layer became solid, sterilized test specimen (dyed wool fabric cut into circular shape of diameter 2 cm) was placed on it. The petri dishes were then incubated for 24 h at room temperature. The clear zones of no growth of bacteria were observed through the bottom of the plate. The width of the clear zone was calculated as follows:

$$W = \frac{T - D}{2}$$

where, W = width of clear zone in cm, T = total diameter of fabric specimen and clear zone, D = diameter of the fabric specimen.

For antifungal test, potato dextrose agar was taken and inoculation was done with standard strain of *Aspergillus niger* (obtained from NCL, Pune, India).

Method-II: 1 mL of nutrient broth was taken and inoculated with one colony of bacteria, *Staphylococcus aureus*. In the same broth, 0.3 mL of

TABLE-3
MAXIMUM WAVELENGTH ABSORPTION VALUES AND R_f VALUES

Dye no.	Dye	Colour of aq. Sol. (0.001 %)	λ_{max}	Colour of spot on TLC	R_f
I	Omega Chrome fast Blue B	Light pink	560	Reddish violet	0.75
II	Omega Chrome Brown EB	Light brown	400	Light brown	0.75
III	Omega Chrome Bordeaux BR	Dark yellow	483	Yellow	0.75
IV	Omega Chrome Brown 2RI	Yellow	410	Light yellow	0.70
V	Omega Chrome Yellow K	Very light yellow	400	Greenish yellow	0.67
VI	Omega Chrome Black S Supra	Light red	545	Dirty bluish grey	0.67
VII	1,2,4, Acid → NW Acid	Pink	550	Light violet	0.88
VIII	1,2,4 Acid → Schaffer's Acid	Light pink	543	Light pink	0.84
IX	1,2,4 Acid → β-Naphthol	Light reddish violet	540	Yellowish grey	0.86
X	Zinc complex of Omega Chrome fast Blue B	Pink	554	Light pink	0.67
XI	Zinc complex of Omega Chrome Brown EB	Light brown	390	Greyish brown	0.60
XII	Zinc complex of Omega Chrome of Bordeaux BR	Light brown	488	Light reddish yellow	0.65
XIII	Zinc complex of Omega Chrome Brown 2RI	Light yellow	440	Greyish yellow	0.90
XIV	Zinc complex of Omega Chrome Yellow K	Very light yellow	351	Greyish light yellow	0.54
XV	Zinc complex of Omega Chrome Black S Supra	Bluish violet	558	Bluish violet	0.77
XVI	Zinc complex of 1,2,4, acid → NW acid	Dark pink	555	Violet	0.84
XVII	Zinc complex of 1,2,4, acid → Schaffer's Acid	Pink	544	Pink (Bluish)	0.72
XVIII	Zinc complex of 1,2,4 acid → β-Naphthol	Reddish violet	553	Light red	0.89

the dye solution was added. It was incubated for 4 h. Sterilized swab stick was taken and dipped in nutrient broth. After squeezing the swab, streaked over the agar plate (Muller Hinten plate) in three directions. This lawn culture was incubated at room temperature for 24 h.

Light fastness: For assessment of light fastness of dyed samples, AATCC test method 16-1964 was employed using Xenon-Arc lamp continuous light. Fabric samples of dimension 2.5 × 1 cm and standard dyeings - AATCC Blue wool light fastness standard samples, were exposed simultaneously under Xenon arc lamp light for sufficient time to produce appreciable fading equal to step 4 of the Grey scale. Colour fastness is then rated in terms of the relative fastness of specimen and standard.

Washing fastness: Washing fastness was tested as per the procedure of ISO II. Each dyed sample was sandwiched between undyed wool sample and white cotton sample and stitched all around. Non-ionic soap solution (5 gpl) (Auxipon NP, Auxichem) was heated to 60°C before introducing the samples. Samples were treated for 0.75 h with material to liquor ratio of 1:50. The samples were rinsed, separated and dried. These samples were evaluated using grey scales both for change in shade of the test samples and staining of the undyed samples.

Colour fastness to dry cleaning: Each dyed sample was sandwiched between undyed wool sample and white cotton sample and stitched all around. The samples were treated with perchloroethylene of commercial dry cleaning grade for 0.5 h at room temperature. Samples were dried in air and evaluated using grey scales both for change in colour of the test samples and staining of the undyed samples.

Colourimetric calculations: The Spectraflash® 300 instrument of Datacolour International was used to determine K/S, L, a* and b* values of the dyed samples. The results are given in Table-7.

RESULTS AND DISCUSSION

The results of the antibacterial tests on different dyes are presented in Table-4 and Table-5. It is seen that the 2:1 zinc complex dyes have prominent antibacterial properties as against the uncomplexed monoazo dyes.

TABLE-4
GROWTH OF BACTERIA IN PRESENCE OF VARIOUS DYES

Dye no.	Dye	Clear zone observed	AA
I	Omega Chrome fast Blue B	No	-ve
II	Omega Chrome Brown EB	No	-ve
III	Omega Chrome Bordeaux BR	No	-ve
IV	Omega Chrome Brown 2RI	No	-ve

Dye no.	Dye	Clear zone observed	AA
V	Omega Chrome Yellow K	No	-ve
VI	Omega Chrome Black S Supra	No	-ve
VII	1,2,4, Acid → NW acid	No	-ve
VIII	1,2,4, Acid → Schaffer's acid	No	-ve
IX	1,2,4 Acid → β-Naphthol	No	-ve
X	Zinc complex of Omega Chrome fast Blue B	Yes	+ve
XI	Zinc complex of Omega Chrome Brown EB	Yes	+ve
XII	Zinc complex of Omega Chrome Bordeaux BR	Yes	+ve
XIII	Zinc complex of Omega Chrome Brown 2RI	Yes	+ve
XIV	Zinc complex of Omega Chrome Yellow K	Yes	+ve
XV	Zinc complex of Omega Chrome Black S Supra	Yes	+ve
XVI	Zinc complex of 1,2,4, acid → NW acid	Yes	+ve
XVII	Zinc complex of 1,2,4, acid → Schaffer's acid	Yes	+ve
XVIII	Zinc complex of 1,2,4 acid → β-Naphthol	Yes	+ve

AA = Antibacterial activity.

TABLE-5
COLONIAL COUNTS OF THE BACTERIA IN PRESENCE OF VARIOUS DYES

Dye no.	Dye	No. of colonies < (cfu units)	AA	Reduction in colonies (%)
I	Zinc complex of Omega Chrome fast Blue B	8	Yes	*ca.* 100
II	Zinc complex of Omega Chrome Brown EB	10^3	Yes	99
III	Zinc complex of Omega Chrome of Bordeaux BR	0	Yes	100
IV	Zinc complex of Omega Chrome Brown 2RI	15	Yes	*ca.* 100
V	Zinc complex of Omega Chrome Yellow K	10^3	Yes	99
VI	Zinc complex of Omega Chrome Black S Supra	70	Yes	*ca.* 100
VII	1,2,4, Acid → NW acid	10^5	No	0
VIII	1,2,4 Acid → Schaffer's acid	10^5	No	0
IX	1,2,4 Acid → β-Naphthol	10^5	No	0
X	Zinc Complex of 1,2,4, acid → NW acid	500	Yes	99.5
XI	Zinc complex of 1,2,4, acid → Schaffer's acid	10^3	Yes	99
XII	Zinc complex of 1,2,4 acid → β-Naphthol	10^3	Yes	99

AA = Antimicrobial activity

TABLE-6
ANTIBACTERIAL TEST OF CONTROL AND DYED WOOL FABRIC (5 % SHADE)

Dye no.	Sample	AA*	TD†	CA‡
	Untreated wool	-	-	-
	Scoured, bleached and definished wool fabric	-	-	-
	Wool fabric padded with zinc sulphate solution	Yes	2.60	0.300
I	Omega Chrome fast Blue B	-	-	-
II	Omega Chrome Brown EB	-	-	-
III	Omega Chrome Bordeaux BR	-	-	-
IV	Omega Chrome Brown 2RI	-	-	-
V	Omega Chrome Yellow K	-	-	-
VI	Omega Chrome Black S supra	-	-	-
VII	1,2,4, Acid → NW acid	-	-	-
VIII	1,2,4, Acid → Schaffer's acid	-	-	-
IX	1,2,4 Acid → β-Naphthol	-	-	-
X	Omega Chrome fast Blue B (post dyeing zinc metallization)	Yes	3.80	0.900
XI	Omega Chrome Brown EB (post dyeing zinc metallization)	Yes	2.50	0.250
XII	Omega Chrome Bordeaux BR (post dyeing zinc metallization)	Yes	4.20	1.100
XIII	Omega Chrome Brown 2RI (post dyeing zinc metallization)	Yes	3.15	0.575
XIV	Omega Chrome Yellow K (post dyeing zinc metallization)	Yes	2.80	0.400
XV	Omega Chrome Black S supra (post dyeing zinc metallization)	Yes	2.50	0.250
X	Omega Chrome fast Blue B (pre metallization with zinc)	Yes	4.50	1.250
XI	Omega Chrome Brown EB (pre metallization with zinc)	Yes	2.70	0.350
XII	Omega Chrome Bordeaux BR (pre metallization with zinc)	Yes	4.20	1.100
XIII	Omega Chrome Brown 2RI (pre metallization with zinc)	Yes	3.50	0.750
XIV	Omega Chrome Yellow K (pre metallization with zinc)	Yes	3.00	0.500
XV	Omega Chrome Black S Supra (pre metallization with zinc)	Yes	3.50	0.750
XVI	Zinc complex of 1,2,4, acid → NW acid (premetallization)	Yes	4.60	1.300
XVII	Zinc complex of 1,2,4, acid → Schaffer's acid (premetallization)	Yes	4.20	1.100
XVIII	Zinc complex of 1,2,4 acid → β-Naphthol (premetallization)	Yes	4.00	1.000

*AA = Antibacterial activity, †TD = Total diameter, ‡CA = Clearance area.

The results of antibacterial properties of the dyed fabric samples are presented in Table-6. To rule out the possibility of wool fabric having inherent antibacterial properties, the untreated wool fabric was also subjected to the antibacterial test. It was observed from the results in Table-6 that in both the cases, antibacterial activity was absent. The undyed bleached wool fabric padded with $ZnSO_4$ solution only was subjected to the antibacterial test. A distinctly clear zone free of bacteria was observed. The width of the clear zone was 0.30 cm indicating antibacterial activity. Thus it was established that wool fabric as such and also after bleaching does not have antibacterial property and the presence of zinc on the fabric imparts resistance against growth of bacteria.

The antimicrobial activity of zinc complexed dyes may be attributed to the presence of these metal ions, which cause precipitation of enzymes or other essential proteins of the cell. As reported in the literature[8,9], the antibacterial action is due to selective interfacing with the synthesis of one of the large-molecule constituents of the cell-the cell wall or proteins or nucleic acids.

The dyes which were synthesized in the laboratory were tested for colouration on wool and all of them gave good colour depth as seen from K/S values reported in Table-7.

TABLE-7
L,a*,b* AND K/S VAUES 0F DYED WOOL FABRIC (1 % SHADE)

Dye no.	Dye	λ_{max}	K/S	L	a*	b*
VII	1,2,4, Acid → NW acid	520	8.4131	32.59	12.56	1.94
VIII	1,2,4, Acid → Schaffer's acid	540	10.4216	27.94	10.89	-11.70
IX	1,2,4 Acid → β-Naphthol	540	12.6993	25.44	10.84	-9.25
XVI	Zinc complex of 1,2,4, acid → NW acid	590	20.2258	19.93	5.38	-18.15
XVII	Zinc complex of 1,2,4, acid → Schaffer's acid	510	9.5557	30.91	13.06	2.32
XVIII	Zinc complex of 1,2,4 acid → β-Naphthol	540	11.4136	28.56	16.08	-9.08

It was observed (Table-8) that light fastness properties of all these dyes were in the range of 4-6, which was quite satisfactory. The high light fastness of these dyes can be attributed to aggregation of dyes within the fibre. In aggregates, less number of dye molecules are exposed to air and hence less accessible to light. The shift in visible absorption maxima is attributable to perturbation of the π-electron density distribution of the dye chromogen which is responsible for the generally high light fastness properties of metallized azo dyes[10]. In general, it could be said that complexing of these dyes with zinc metal definitely improved the light fastness characteristics.

The washing fastness as well as dry cleaning fastness of wool samples dyed with zinc complexed dyes remained unaltered and in the range of 4-5 *i.e.* very good to excellent (Table-8).

TABLE-8
FASTNESS PROPERTIES OF WOOL FABRIC DYED WITH UNMETALLIZED DYES AND ZINC COMPLEXED DYES (1 % SHADE)

Dye no.	Dye	Washing fastness			Dry cleaning fastness			Light fastness
		Change of shade	Staining on wool	Staining on cotton	Change of shade	Staining on wool	Staining on cotton	
VII	1,2,4, Acid → NW acid	5	4-5	5	5	5	5	3-4
VIII	1,2,4, Acid → Schaffer's acid	5	4-5	5	5	5	5	3-4
IX	1,2,4 Acid → β-Naphthol	5	4-5	5	5	5	5	3-4
XVI	Zinc complex of 1,2,4, acid → NW acid	5	4-5	5	5	5	5	4-5
XVII	Zinc complex of 1,2,4, acid → Schaffer's acid	5	4-5	5	5	5	5	5-6
XVIII	Zinc complex of 1,2,4 acid → β-Naphthol	5	4-5	5	5	5	5	4-5

Conclusion

Zinc salts can be successfully used for complexing with monoazo dyes in post-metallization dyeing process to impart antimicrobial property. Pre-metallized zinc complex dyes were found to exhibit antimicrobial properties. As long as these dyes are on the wool fabric, its antibacterial property continues to last giving a new route of obtaining durable antibacterial properties for woolen material.

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