



ISSN No: 0975-7384  
CODEN(USA): JCPRC5

*J. Chem. Pharm. Res.*, 2010, 2(6):78-85

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## **Studies on synthesis and dyeing performance of disperse azo dyes based on schiff base of ninhydrin and 4-amino phenol**

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### **ABSTRACT**

*Some new disperse azo dyes based on Schiff base of ninhydrin and 4-amino phenol were prepared by coupling of various diazo solution of benzene derivatives. The resultant dyes were characterized by elemental analyses as well as IR and NMR spectral studies. The UV-Visible spectral data have also been discussed in terms of structural property relationship. All the disperse azo dyes were applied on polyester textile fibers. The percentage dye bath exhaustion and fixation on the polyester fibers have been found to be very good. The dyed fabrics showed moderate to very good light fastness and washing fastness properties.*

**Keywords:-** Ninhydrin, Schiff bases, Disperse azo dyes, Polyester fiber, Fastness.

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### **INTRODUCTION**

The chemistry of ninhydrin has been studied extensively. Much of the work has been directed toward the reaction of amines with ninhydrin[1,2]. Ninhydrin is a triketo compound used in the detection and estimation of amino acids. The reaction between ninhydrin and amino acids has been studied extensively[3]. The glycine and ninhydrin reaction is an example of nucleophilic addition of amino to carbonyl group and proceeds to the formation of Schiff bases[4]. These Schiff base may be having good biological activities because ninhydrin is it self an important reagent in bimolecular reaction. The area for synthesis of azo dyes bases on these Schiff bases has not been developed so far. Hence it was to explore the studies of azo dyes based on these Schiff base.

The present paper describes the synthesis of the Schiff base (**3**) of ninhydrin (**1**) and 4-amino phenol (**2**). Thus, Schiff base (**3**) was synthesized as shown in the reaction scheme. In the next stage, Schiff base (**3**) was coupled with the dizonium solution of various aromatic amines (**4a-q**) to yield monoazo dyes (**5a-q**). The resultant dyes were characterized by elemental analyses as

well as IR and NMR spectral studies. The UV-Visible spectral data have also been discussed in terms of structural property relationship. All the disperse azo dyes were applied on polyester textile fibers.

## EXPERIMENTAL SECTION

Ninhydrin and absolute ethanol, which were used, were of A.R. grade. All the other chemicals used were of laboratory grade and were further purified by crystallization. Melting points were determined by the open capillary method and were uncorrected. The UV-Visible absorption spectra were measured in dimethylformamide (DMF) on a SHIMADZU A-20 spectrophotometer. The UV-Visible spectra of all dyes were obtained for solution ( $1.0 \times 10^{-3}$  mg/ml) prepared. The C, H, N contents of all the dyes were estimated by Thermofinigan Elemental analyzer (Italy). IR spectra were recorded (KBr disc) on a FTIR-8400 Shimadzu IR spectrophotometer.  $^1\text{H}$  NMR Spectra of all dyes were obtained on Bruker ultrashield 300 MHz spectrophotometer.

### 2-[(4-hydroxyphenyl)imino]-1H-indene-1,3(2H)-dione (3)

Schiff base containing C=N bond were synthesized according to the method of the various Schiff base derivatives available in the literature[5-7].

The schiff base has been synthesized by adding the ethanolic solution of Ninhydrin (0.1 mole) with ethanolic solution of 4-amino phenol (0.1 mole) in equimolar ratio. The reaction mixture was then refluxed on a water bath for about 1-2 hours. The condensation product was filtered, thoroughly washed with ethanol, re-crystallized and dried. TLC using silica gel monitored the purity of the synthesized compounds. The yield of the product was 85% and the melting point was 220°C

### Synthesis of Azo dyes (5a-q)

Procedures for the synthesis of azo dyes from this type of phenols are well invented in the literature[8-10].

### Preparation of the Diazonium Solution (4a-q)

Amines (0.02 mole)(a-q) the mixture of concentrated hydrochloric acid and water were dissolved in a conical flask. A thermometer was placed in solution and the flask in a bath of crushed ice. The solution was stirred until the temperature of the solution falls below 5°C. Dissolve Sodium nitrite (1.378 gm) in water (13.8 ml). It was cooled to 0°C with the help of the ice bath. Then the sodium nitrite solution (2-3 ml at a time) added gradually in to the cold aniline hydrochloride solution, with good stringing. The temperature was kept between 0°-5°C. The reaction mixture shows the positive test of nitrous acid on starch iodide paper. (i.e. blue colour is obtained on the potassium iodide-starch paper).

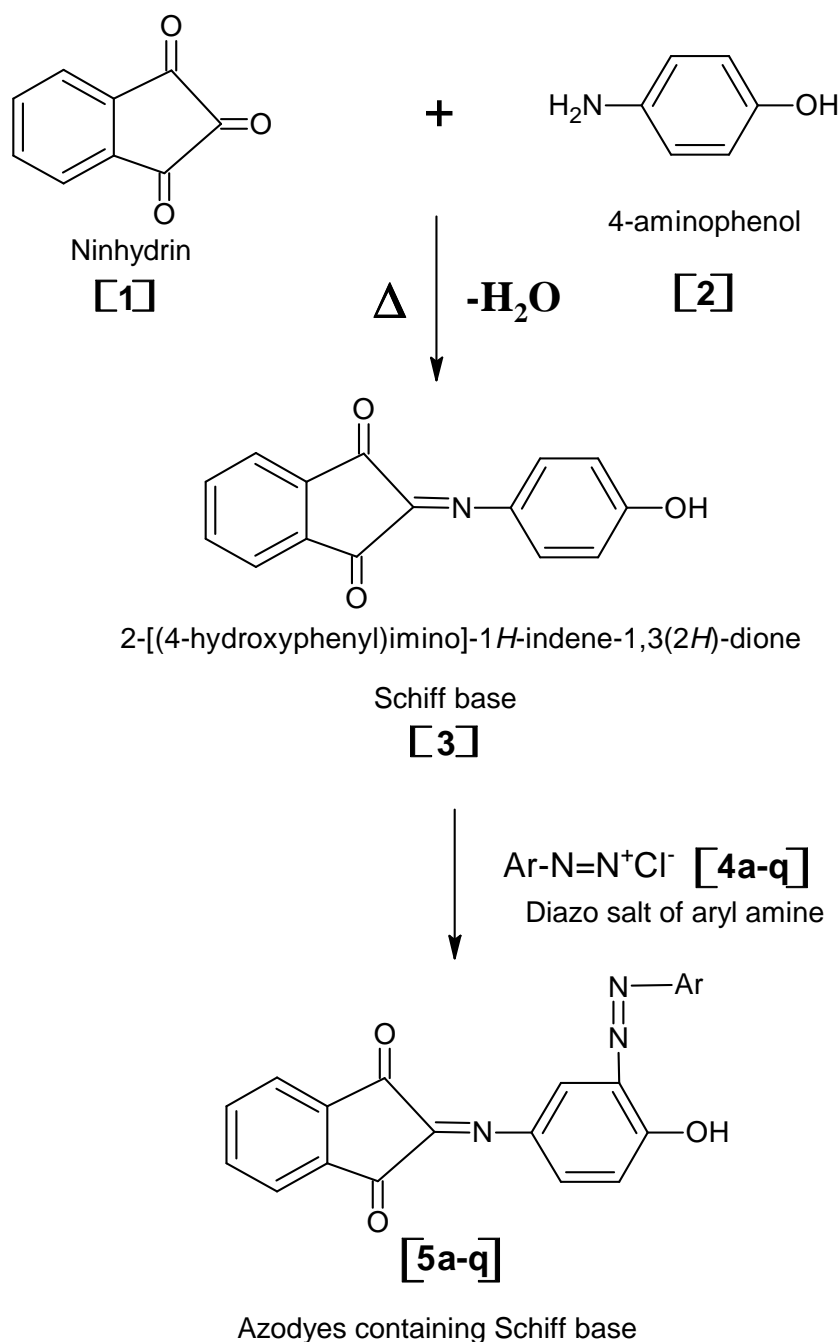
### Preparation of the Schiff base Solution

A solution of Schiff base (3) (2-[(4-hydroxyphenyl)imino]-1H-indene-1,3(2H)-dione) (3) (0.02 mole, 5.025 gm) in the solution of sodium hydroxide (0.8 gm in 22.1 ml water) was prepared in a 250-ml beaker. The mixture was stirred for few minutes because Schiff base was dissolve sodium hydroxide solution. Cool the solution to 5°C by immersion in an ice bath.

### Formation of the dye

Stir the Schiff base (3) solution vigorously and add the diazonium salt solution very slowly, maintaining the temperature between 0°-5°C. The mixture was then stirred for 1hr. at 0°-5°C.

After completion of the reaction, the precipitates was filtered, washed with water and dried to get colored precipitates. When it was crystallized from absolute ethanol. The yield of the dye was 60 to 80% and the melting point was uncorrected.



Where Ar = Benzene derivatives (Table No.)

Scheme-1. Synthesis of Azo dyes

**Synthesis of the Schiff base (3)**

The same procedure was used for the preparation of dyes (5a-q) using various amines (a-q). The whole process for the synthesis is shown in Scheme-1. The characterization data of dyes (5a-q) are given in Table-1.

**Table 1. Physical data for azo dyes**

Dye No.	Coupling Component	Yield (%)	M.P. (°C)	Mol. Formul (Mol.Wt.)	Elemental analysis : found(calcd.)		
					C %	H %	N %
5a	Aniline	68	113	C <sub>21</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub> (355.35)	70.9(70.98)	3.6(3.69)	11.7(11.83)
5b	4-nitro aniline	75	127	C <sub>21</sub> H <sub>12</sub> N <sub>4</sub> O <sub>5</sub> (400.34)	62.4(63.00)	2.8(3.02)	13.5(13.99)
5c	3-nitro aniline	68	132	C <sub>21</sub> H <sub>12</sub> N <sub>4</sub> O <sub>5</sub> (400.34)	62.9(63.00)	3.0(3.02)	13.8(13.99)
5d	2-nitro aniline	70	116	C <sub>21</sub> H <sub>12</sub> N <sub>4</sub> O <sub>5</sub> (400.34)	62.8(63.00)	2.9(3.02)	13.7(13.99)
5e	4-bromo aniline	78	126	C <sub>21</sub> H <sub>12</sub> BrN <sub>3</sub> O <sub>3</sub> (434.24)	57.9(58.08)	2.7(2.79)	18.3(18.40)
5f	3-chloro aniline	62	102	C <sub>21</sub> H <sub>12</sub> ClN <sub>3</sub> O <sub>3</sub> (389.79)	64.6(64.71)	3.0(3.10)	10.7(10.78)
5g	4- chloro aniline	60	128	C <sub>21</sub> H <sub>12</sub> ClN <sub>3</sub> O <sub>3</sub> (389.79)	64.6(64.71)	3.0(3.10)	10.7(10.78)
5h	4-amino phenol	70	208	C <sub>21</sub> H <sub>13</sub> N <sub>3</sub> O <sub>4</sub> (371.34)	67.8(67.92)	3.5(3.53)	11.2(11.32)
5i	3-amino phenol	65	229	C <sub>21</sub> H <sub>13</sub> N <sub>3</sub> O <sub>4</sub> (371.34)	67.8(67.92)	3.4(3.53)	11.2(11.32)
5j	2-amino phenol	60	198	C <sub>21</sub> H <sub>13</sub> N <sub>3</sub> O <sub>4</sub> (371.34)	67.8(67.92)	3.4(3.53)	11.2(11.32)
5k	4-toludine	72	184	C <sub>22</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> (369.37)	71.5(71.54)	4.0(4.09)	11.3(11.38)
5l	3-toludine	68	190	C <sub>22</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> (369.37)	71.5(71.54)	4.0(4.09)	11.2(11.38)
5m	2-toludine	64	172	C <sub>22</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> (369.37)	71.5(71.54)	4.0(4.09)	11.3(11.38)
5n	4-anisidine	62	121	C <sub>22</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub> (385.37)	68.5(68.57)	3.9(3.92)	10.8(10.90)
5o	3-anisidine	65	138	C <sub>22</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub> (385.37)	68.5(68.57)	3.8(3.92)	10.9(10.90)
5p	2-anisidine	70	112	C <sub>22</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub> (385.37)	68.5(68.57)	3.8(3.92)	10.8(10.90)
5q	α-naphthyl amine	55	107	C <sub>25</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub> (404.40)	74.0(74.07)	3.7(3.73)	10.3(10.36)

### Dyeing of polyester fabric

Dyeing of polyester fabric was performed using a procedure reported in the literature[11-13].

**Pretreatment of Polyester:** Polyester pattern (2.0 gm) was introduced into at conical flask containing distilled water (100 ml). 2/3 portion of the flask was immersed into a thermostate bath. Temperature was raised and maintained at 80° C for 10 minutes. The polyester pattern was then taken out of the flask, squeezed very well, dried and subsequently used for dyeing.

**Preparation of Dye Bath:** For 2% dyeing, a dye under study (40 mg) was dissolved in possible minimum quantity of miscible solvent like DMF. To a 250 ml conical flask containing the solution of dispersing agent (i.e.dodamal) 100 mg in distilled water to obtain a fine aqueous dispersion of the dye. The dye solution was then added with continuous stirring into a dye pot containing the solution of dispersing agent. The total volume of the solution in the dye bath was 100 ml. Thus, the MLR was maintained 1:50.

**Dyeing:** The dye bath was set at 60° C and this temperature was maintained for 20 minutes. The pretreated polyester fabric (2.0 gm) was introduced into the dye bath. The temperature was then raised up to 70° C. The temperature from 70° C to 130° C was raised within 1 hour at the rate of 1° C per 1 minute. Dyeing was carried out at this temperature for 1 hour. After 1 hour, the dye bath was cooled. The dyed polyester pattern was washed several times with cold water (100 ml). This water was collected in a volumetric flask (250 ml) containing DMF (40 ml). The combined solution of the residual dye liquor collected from the dye bath and washing water were then diluted to 250 ml with water. After diluting 25 ml of this solution was pipetted out for further dilution to 50 ml with water. 1ml of this consequent solution was further diluted to 10 ml with DMF. The absorbance of this diluted solution was measured.

Thus, the dyed polyester pattern was obtained. It was then rinsed and scoured in a detergent solution (Lissapol, 100 ml, 0.2%) at 50° C for 25 minutes. The dyes polyester fabric pattern was rinsed again and dried.

Colour fastness tests : Fastness to light was assessed in accordance with BS:1006-1978. The wash fastness was tested in accordance with IS:765-1979.

Exhaustion and fixation: The percentage dye bath exhaustion and fixation of the dyed fabric were calculated by known methods[14-16].

## RESULTS AND DISCUSSION

(2-[(4-hydroxyphenyl)imino]-1H-indene-1,3(2H)-dione) (**3**) has been synthesized by adding the methanolic solution of ninhydrin and 4-amino phenol in equimolar ratio. The reaction mixture was refluxed on a water bath for about 1-2 hours. Amines (**a-q**) in the mixture of concentrated hydrochloric acid and water were dissolved the solution was stirred until the temperature of the solution falls below 5° C. Sodium nitrite solution was cooled to 0° C and added gradually in to the cold aniline hydrochloride solution with good stringing the temperature was kept between 0°-5° C. Thus, preparation of diazonium solution (**4a-q**). (2-[(4-hydroxyphenyl)imino]-1H-indene-1,3(2H)-dione) (**3**) was dissolve sodium hydroxide solution. Cool the solution to 5° C. Stir the schiff base (**3**) solution vigorously and add the dizonium salt solution (**4a-q**) very slowly, maintaining the temperature between 0°-5° C. After completion of the reaction, to get colored dyes (**5a-q**) precipitates.

### Physical properties of dyes

All melting points are uncorrected. The dyes was crystallized from absolute ethanol. The yield of the dye was 60% to 80 %. The purity of the dyes were checked by TLC using ethyl-benzene (1:4) as the solvent system. When adsorbed onto silica chromatography plates, the dyes produced a single colour spot.

### Infrared spectra

All the disperse azo dyes possess important characteristic functional groups like azo group (-N=N-), Phenolic group (-OH), Ketones group (C=O), Schiff bases bond (-C=N-), and aromatic nucleus etc.

Aromatic C—H stretching bands occur between 3212-3389 cm<sup>-1</sup> in all the spectra. Phenolic (-OH) group remains unchanged during the reaction. Each of these spectra is observed in the rang of 3019-3098 cm<sup>-1</sup> broad band as the indication of presence of phenolic group (-O-H) in all there disperse azo dyes. In the present study, the disperse azo dyes give an absorption band in the region of 1514-1599 cm<sup>-1</sup> It shows the presence of an azo group (-N=N-) in each of the disperse azo dyes molecules. Infrared spectra of all the disperse azo dyes, an absorption band is observed in the region of 1605 to 1686 cm<sup>-1</sup> due to C=N (schiff base bond) in all the dyes.

The other noteworthy absorption bands that are observed in these spectra are stated below:

The bands around 1472 cm<sup>-1</sup> and 1346 cm<sup>-1</sup> observed due to -NO<sub>2</sub> group for the **5b**, **5c** and **5d**. The band around 1284 cm<sup>-1</sup> observed due to -NH<sub>2</sub> group for the **5h**, **5i** and **5j**. The band around 2812 cm<sup>-1</sup> observed in the spectra of **5n**, **5o** and **5p** dyes which might be due to -O-CH<sub>3</sub> group.

**<sup>1</sup>H NMR spectra**

Nuclear magnetic resonance (NMR) spectroscopy is of great value in the structural elucidation of synthetic dyes than ultraviolet or infrared spectroscopy in terms of structural information derived from the spectrum. These NMR spectra were taken by using Acetonitrile-d<sub>3</sub> solvent. The delta values are given in ppm. Observation of all these <sup>1</sup>H NMR spectra indicates that these spectra are almost identical due to the fact that all contain signals for phenolic hydroxyl group (Ar-OH) protons and aromatic protons. In all <sup>1</sup>H NMR spectra, a signal appeared near  $\delta$  1.93(5) to  $\delta$  1.95(5) can be assigned to a proton of acetonitrile-d<sub>3</sub> as a solvent[17-18].

**Table 2. Colour shad,  $\lambda_{\max}$  nm, % Exha., % Fixa., Wash and Light fastness data**

Dye No.	Colour shade On polyester	Absorption $\lambda_{\max}$ nm	log $\epsilon$	Exhaustion %	Fixation %	Fastness properties	
						washing	light
5a	Fawn Dream	398	1.8325	59.45	69.05	2	3
5b	Yellow Charm	406	1.8751	56.65	78.02	3	4
5c	Yellow Loris	413	1.9638	61.45	74.73	3	4
5d	Light Ochre	418	1.9912	54.50	79.59	2	3
5e	Brandy	402	1.5052	52.15	80.15	3	3
5f	Grand Canyon	395	1.9138	63.33	77.02	2-3	3-4
5g	Ginger Bread	380	1.4472	62.83	79.66	2	4
5h	Rustic Charm	403	1.9294	61.35	79.26	3	3
5i	Copper Leaf	420	1.5563	56.28	78.23	3	4
5j	Brown Sugar	425	1.8975	66.15	71.50	2	3-4
5k	Light Biscuit	437	2.0212	66.35	72.61	2-3	3
5l	Red Marble	428	1.9494	63.47	72.23	3	3-4
5m	Rustic Pottery	433	1.8751	65.08	65.50	2	4
5n	Rich Tan	427	1.8573	63.50	75.63	3	4
5o	Warm Glow	432	1.9138	66.75	72.87	2	3
5p	Balsam Brown	410	1.8388	58.95	71.20	3-4	4
5q	Ivory	397	1.6532	63.68	72.32	3	3-4

The data of important signals observed in all disperse azo dyes spectra are given below:

**5a:** 8.213 (s, 1H, -OH), 6.734 – 7.946 (m, 12H, Ar-H) **5b:** 8.145 (s, 1H, -OH), 6.428 – 8.245 (m, 11H, Ar-H) **5c:** 7.837 (s, 1H, -OH), 6.784 – 7.969 (m, 11H, Ar-H) **5d:** 8.312 (s, 1H, -OH), 6.861 – 7.849 (m, 11H, Ar-H) **5e:** 8.346 (s, 1H, -OH), 6.524 – 8.327 (m, 11H, Ar-H) **5f:** 7.961(s, 1H, -OH), 6.631 – 8.174 (m, 11H, Ar-H) **5g:** 7.997 (s, 1H, -OH), 6.017 – 7.586 (m, 11H, Ar-H) **5h:** 8.147 (s, 1H, -OH), 8.175 (s, 1H, -OH), 6.367 – 7.627 (m, 11H, Ar-H) **5i:** 7.998 (s, 1H, -OH), 7.998 (s, 1H, -OH), 6.379 – 7.751 (m, 11H, Ar-H) **5j:** 8.167 (s, 1H, -OH), 8.143 (s, 1H, -OH), 6.460 – 8.261 (m, 11H, Ar-H) **5k:** 2.534 (s, 3H, -CH<sub>3</sub>), 8.167 (s, 1H, -OH), 6.749 – 7.816 (m, 11H, Ar-H) **5l:** 2.467 (s, 3H, -CH<sub>3</sub>), 7.964 (s, 1H, -OH), 6.334 – 7.872 (m, 11H, Ar-H) **5m:** 2.485 (s, 3H, -CH<sub>3</sub>), 8.104 (s, 1H, -OH), 6.540 – 7.864 (m, 11H, Ar-H) **5n:** 3.264 (s, 3H, -OCH<sub>3</sub>), 7.968 (s, 1H, -OH), 6.240 – 7.846 (m, 11H, Ar-H) **5o:** 3.279 (s, 3H, -OCH<sub>3</sub>), 7.924 (s, 1H, -OH), 6.734 – 7.946 (m, 11H, Ar-H) **5p:** 3.281 (s, 3H, -OCH<sub>3</sub>), 8.006 (s, 1H, -OH), 6.561 – 8.237 (m, 11H, Ar-H) **5q:** 8.106 (s, 1H, -OH), 6.267 – 8.314 (m, 14H, Ar-H)

**UV-Visible spectra**

The disperse azo dyes dissolved in DMF (N, N, -dimethyl formamide) as a solvent. Visible spectra of all disperse azo dyes were obtained for solution (1.0 x 10<sup>-3</sup> mg./ml.) prepared. The concentration of the dye in the solution was 1.0x10<sup>-3</sup> mg./ml. From the visible spectrum, the values of  $\lambda_{\max}$  and the absorbance corresponding to the  $\lambda_{\max}$  were read and molar extinction coefficient ( $\epsilon$ ) values are estimated using Lambert-Beer's equation. Spectral data are reported in Tables: II. Examination of all data and spectral curves reveals the following characteristics. The

molar extinction coefficient ( $\epsilon$ ) of all the dyes is of the order of  $10^4$ . It has been observed that all dyes absorb at higher wavelength.

### Dyeing properties of dyes

The disperse dyes (**5a-q**) were applied at 2% depth on polyester fabrics. The dyes gave excellent uniformity of colouration on polyester fabrics and the overall fastness properties of the dyes are shown in Tables II. These dyes gave yellow to brown hues with brighter and deeper shades with high tinctorial strength and excellent levelness on the fabric. The variation in the shades of the fabric results from both the nature and position of the substituent present on the diazotized compound. The results of the exhaustion of the dye bath and the fixation of the dyed fabric are given in Table II.

### CONCLUSION

Examination of the percentage dye bath exhaustion data of all disperse azo dyes shows good dye bath exhaustion. All disperse azo dyes show percentage dye bath exhaustion ranging from 52 to 67 %. The percentage fixation of disperse azo dyes shows better fixation. Whatever amount of dye had exhausted from the dye bath had got fixed on the fiber. So it resulted in good dye bath exhaustion and almost 66 to 81 % fixation. This is the striking feature of these disperse azo dyes.

The light and wash fastness of all patterns dyed with disperse azo dyes show fairly good to very good fastness properties. The shades of the fabric given in the thesis are based on 'Nerolac Paint Shade Card' and 'Asian Paint Shade Card'.

### Acknowledgment

We are thankful to Director of our R. R. Mehta college of Science, palanpur for providing laboratory facilities. My deep hearted desire to thank especially Dr. P. S. Anand, Deputy Director, Central Salt and Marine Chemical Research institute, Bhavanagar, Ramesh P. Parmar, Q. C. Senior officer, Disman Pharmaceutical, Ahmedabad, for their valuable guidance and ever willing help investigation.

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