Azoic Dyeing: Forgotten Art?

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By:
Ashok Athalye,
Arindam Chakrabarti
&
Hashmukh Tailor

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Atul Ltd. (Colors Division), Atul, Valsad, Gujarat, India

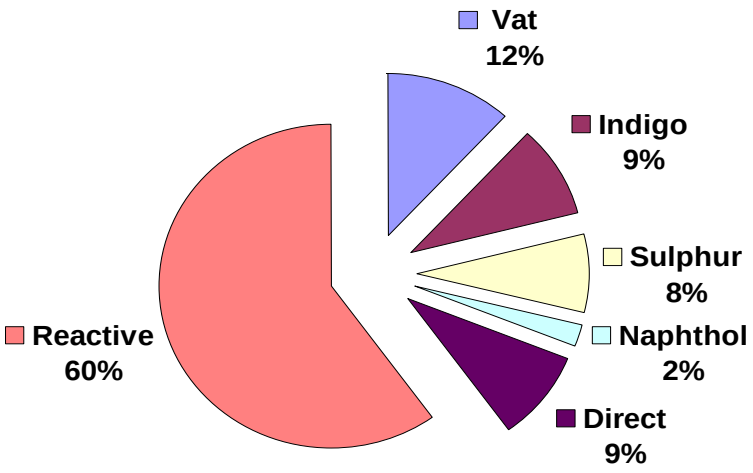
Introduction

In India, Textiles is a part of our ancient heritage and traditions. It is also an integral part of our social and cultural milieu. The roots of textiles industry in general and colouration industry in particular are buried deep in history, going back several centuries. Time to time, the industry has added its strength by incorporating modernisation, skillful human resources meeting the changing market challenges, machines and product ranges. Presently, with its intrinsic strength and with the aid of several promoting factors, the Indian Textile industry has been able to make its mark on the global scenario, penetrating the market both in terms of range of products and countries.

The textile industry comprises a diverse, fragmented group of establishments that receive and prepare fibres, transform into yarn, convert the yarn into fabric and then dye at various stages of garment manufacturing. The processing of such a huge volume of fabric and clothing is carried out in different locations belonging to the hand processing units, composite mills and independent process houses of various sizes. The colouration of textiles is an important aspect of the production process and adds value to it, be it by dyeing or printing. So, the contribution of dyestuff industry in wet processing operations is enormous. Atul (Colors Division) is one of the pioneers in dyestuff manufacturing era in India and produce all classes / types of dyestuffs, specialty pigments and textile auxiliaries.

Cotton is the backbone of the world's textile trade. It has many qualities and countless end uses, which makes it one of the most abundantly used textile fibres in the world. Cotton is widely used due to its physio-chemical properties like feel and comfort to wear to human body. It is processed either in its natural or regenerated forms like viscose, modal, lyocell, etc., as self or in blend with synthetics or other innovative, eco friendly fibres like Bamboo, Soya bean, Milk, Paper, Charcoal, etc. Out of the various classes of dyestuffs used for cellulosic dyeing, though reactive dyes followed by vat dyes enjoy the major share, the contribution of Azoic / Napthol – Base is very important and very special owing to their application process, production of very deep & bright shades, energy conservation, good light / bleach / wash fastness properties and cost economies.

The global consumption share of different types of dyestuff for cellulosic colouration is as given below



Dyestuffs for Cellulosic colouration

Naphthols and Bases

Azoic dyes are insoluble azo dyestuffs, which are produced on the fibre by applying a Naphthol to the fibre and then combining it with a diazotized base or salt at a low temperature to produce an insoluble dye molecule within the fibre. The technique of dyeing is unique, in that the final colour is controlled by the choice of the diazoic and coupling components. Naphthol dyes are classified as fast dyes and a number of bright shades could be produced. Azoic combinations are still the only class of dye that can produce very deep bright yellow, bright orange, red, scarlet and Bordeaux shades.

Naphthols

Naphthols are 'Azoic Coupling Components'. These are mainly the arylides of BON acid (β-Oxynapthoic acid), in addition to a few aceto-acetic acids and o-hydroxy carboxylic acids of anthracene, carbazole, benzo carbazole and dibenzofuran. The Naphthols are soluble in alkaline solution and substantive to cotton, particularly in the presence of salt. They are soluble in dilute NaOH solution and form the corresponding naphtholate ion. These relatively small molecules are of only low to moderate substantivity for cotton, but they diffuse rapidly into the fibres. In general, the higher the substantivity the better the rubbing fastness as less azo pigment forms on the fibre surfaces. The naphtholate ions are always coplanar and preferably have elongated molecular structures. They behave essentially as colourless, low molecular weight direct dyes. The

substantivity increases with increase in the molecular size of the naphtholate ion, but the diffusion rate in the fibres and solubility in dilute aqueous alkali decreases. Addition of salt promotes better exhaustion of the bath, more being needed for Naphthols of lower substantivity.

Bases

Fast Colour Bases are 'Azoic Diazo Components'. They are mainly aniline derivatives substituted with nitro, methoxy, ethoxy, halogen benzanilido groups by themselves or in combination. These Fast Colour Bases require diazotisation. This usually involves reaction of the primary aromatic amine in acidic solution or dispersion with sodium nitrite, below room temperature. Successful diazotisation requires careful weighing of all the chemicals and following of supplier's recommendations. Diazotisation of a primary aromatic amine is often difficult and solutions of diazonium ions are inherently unstable. They undergo decomposition even at low temperature and particularly on exposure to light. Storing prepared diazonium ion solutions is not usually possible.

General mechanism of dyeing

- Dissolution of the naphthol component.
- Exhaustion of the naphthol solution onto the substrate or absorption of the naphtholate ion by the cellulose.
- Removal of excess naphthol from the material by squeezing / partial hydroextraction.
- Diazotization of the base component.
- Development or, treatment with the diazonium ion solution to bring about coupling.
- Neutralisation, Soaping at the boil to remove superficial pigment, followed by rinsing and drying.

TULATHOL / TULABASE – Napthol / Base offered by Atul

Atul Ltd., one of the pioneers of dyestuff manufacturing company offers TULATHOL (Azoic coupling component) and TULABASE (Azoic diazo component) - the trade names of Naphthols and Bases respectively. The detailed Standard Operating Procedure for application of TULATHOL / TULABASE on cellulosic substrate is appended below:

A. *Bath A: Preparation of TULATHOL Solution:*

TULATHOL : X parts / litre
TULACHEM Wettex TR : X parts / litre
Caustic Soda (62ºTw) (Part / Litre) : As per Table 1

TULATHOL is pasted with anionic wetting and dye disaggregating agent (Tulachem Wettex TR) and a little water into a smooth paste. Caustic Soda (62ºTw) solution is added with stirring. Hot water containing 1 ml of Caustic soda (62ºTw) solution per litre is then added with continuous stirring. If the solution is not clear, it is boiled till it becomes clear. Make up the required volume.

Table – 1:

TULATHOL Name	gm.	Tulachem Wettex TR (gms.)	Caustic Soda (62°Tw) (ml)
AS-G	1	1	3.0
AS	1	1	1.5
AS-TR	1	1.25	2.0
AS-SW	1	1.25	3.8
AS-D	1	1	1.5
AS-BO	1	1	2.75
AS-BS	1	1	1.5
AS-OL	1	1	1.5

B. *Bath B: Method of Diazotisation of TULABASE:*

Method: 1
[Used for Diazotising TULABASES, whose hydrochlorides are easily soluble in water]

TULABASE : Y parts / litre
Hydrochloric acid (32 ºTw) (Part / Litre) : As per Table 2
Sodium Nitrite (Part / Litre) : As per Table 2
Sodium acetate (crystals) (Part / Litre) : As per Table 2
Acetic acid (50%) (Part / Litre) : As per Table 2

TULABASE is pasted with HCl and little cold water. Hot or cold water is added with stirring. The solution is then cooled to 10 ºC with ice and the Sodium Nitrite solution (1: 1) is added with vigorous stirring, maintaining the temperature in the range of 10-15 ºC with ice. After keeping the solution for 20 mins., the excess HCl is neutralized with Sodium Acetate crystals. Then, Acetic acid is added. The solution is then filtered and made up to the required volume depending on the concentration of TULABASE required.

Table – 2:

TULABASE		Water	Diazoti-sing temp.	HCl (32°Tw)	Sodium nitrite	Sodium acetate	Acetic acid (50%)	Optimum pH
Name	gm.	ml.	°C	ml.	gm.	gm.	ml.	
Yellow GC	1	5*	10	1.2	0.5	1.0	0.75	4.0 – 5.0
Orange GC	1	5*	10	1.2	0.5	1.0	0.75	4.0 – 5.0
Scarlet G	1	20#	12	2.0	0.5	1.0	0.75	4.0 – 5.0
Scarlet RC	1	20	12	1.0	0.4	0.75	0.50	4.0 – 5.0
Red RC / R	1	10*	12	1.0	0.5	0.75	0.30	5.5 – 6.5
Garnet GBC	1	15	5	1.2	0.32	1.25	-	4.0 – 5.0
* - Hot water, # - Boiling water								

Method: 2

[Used for Diazotising TULABASES, whose hydrochlorides are not easily soluble in water]

TULABASE : Y parts / litre
Sodium Nitrite (Part / Litre) : As per Table 3
Hydrochloric acid (32 ºTw) (Part / Litre) : As per Table 3
Sodium acetate (crystals) (Part / Litre) : As per Table 3
Acetic acid (50%) (Part / Litre) : As per Table 3

TULABASE is pasted with a little water and sodium nitrite solution (1:1) is then added. Hot or cold water is added with stirring. The mixture is then added to a solution of HCl (32 ºTw), with continuous stirring, maintaining the temperature in the range of 10-15 ºC with ice. After keeping the solution for 20 mins, the excess HCl is neutralized with sodium acetate crystals. Then acetic acid is added. The solution is then filtered and made up to the required volume depending on the concentration of TULABASE required.

Table – 3:

TULABASE		Water	Diazoti-sing temp.	Sodium nitrite	HCl (32°Tw)	Sodium acetate	Acetic acid (50%)	Optimum pH
Name	gm.	ml.	gm.	ml.	ml.	gm.	ml.	
Red B	1	1.5*	15	0.5	1.75	0.85	0.75	4.0 – 5.0
Bordeaux GP	1	2.0*	15	0.5	1.75	0.85	0.75	4.0 – 5.0
* - Hot water								

C. Dyeing process:

The dyeing process consists of two stages: (a) Impregnation & (b) Development.

In the first stage, the substrate is impregnated with TULATHOL solution and in the second stage; it is developed with diazotized TULABASE solution. The later combines chemically with TULATHOL absorbed by the fibre to give an insoluble dye on the substrate.

- Add Common salt (15-20 g/l) in bath A & then enter RFD substrate (MLR - 1: 20)
- Run for 30 mins. at room temperature
- Squeeze well and open well the substrate
- Add Common salt (25 g/l) in bath B and enter the substrate (MLR - 1: 20)
- Run for 30 mins. at room temperature
- Squeeze well and open well the substrate
- Give thorough cold wash followed by hot wash
- Neutralize with HCl (32 ºTw) – 3 ml/l followed by cold wash
- Soap at 95ºC using TULACHEM Texwash DET (0.5 – 1.0 g/l) and Soda ash (2.0 g/l) for 20 mins. [Soaping temperature may vary depending on nature of TULATHOL/TULABASE combination]
- Hot wash
- Cold wash
- Dry

Notes / Precautions:

1. The alkalinity of the TULATHOL bath should not drop below the prescribed limit, otherwise naphthols may be precipitated.
2. In case of TULATHOL AS-SW, 10 g/l of common salt and in case of TULATHOL AS-G; 15 g/l of common salt should be used.
3. Common Salt should be added just before impregnation of the substrate. Use of excess salt in naphthol bath may result into precipitation of the bath.
4. Maintaining desired temperature is very important in base preparation step, otherwise proper diazotisation would not take place.
5. For complete diazotization, an excess of HCl must be present throughout the diazotization, the acidity is tested by spotting the diazo solution on congo red test paper which would develop deep blue colour. In addition, excess of nitrous acid must also be

present which is detected by spotting the diazo solution on starch iodide test paper, which would develop a dark brown to deep blue black colour.

6. Sodium acetate must be added to the developing bath just before use, otherwise base would become unstable due to fall in concentration of HCl.
7. In case of TULABASE Scarlet G, paste it with HCl and then add boiling water to dissolve it completely. Cool and add sodium nitrite slowly with stirring.
8. Only 10 g/l of common salt should be added to the developing bath prepared from TULABASE Garnet GBC.
9. The TULATHOL impregnated material should be protected from water spots, acid fumes, steam, chlorine fumes and direct sunlight. The development should be carried out as soon as possible.
10. After development, the material should be rinsed without delay, otherwise the mechanically held excess developing liquor would undergo some decomposition and cause deposition of dark coloured spots, which are difficult to remove.

Role of different important chemicals:

(a) Wetting agent

The purpose of adding wetting agent [like TULACHEM Wettex TR or Turkey Red Oil (TRO)] to TULATHOLS is to wet out and disperse the dry TULATHOLS so that the caustic soda can easily react with them. The other functions are as follows:

(i) to prevent crystallisation of TULATHOL from the solution,

(ii) to improve leveling on the fibre,

(iii) to assist in wetting of the material and

(iv) to assist in penetrating the TULATHOL molecules into the material.

(b) Caustic Soda

Certain quantity of caustic soda is necessary to convert the insoluble TULATHOL into the soluble sodium salt. A further minimum concentration of caustic soda is required to keep the sodium salt of TULATHOL in solution. More than specified amount of caustic soda is undesirable as it would tend to hydrolyse the TULATHOL and / or precipitate it from the solution.

(c) Common Salt

The substantivity of TULATHOLS on cotton is increased by the addition of common salt to the bath. Such addition should be made to achieve greater economy in application and to produce better fastness to rubbing. Too much common salt may lead to precipitation of the TULATHOL. Salt should be added just before the impregnation.

(d) Hydrochloric acid

HCl is used for dissolution of TULABASE and to produce nitrous acid in diazotization phase.

(e) Sodium Nitrite

It helps to produce nitrous acid in diazotization phase.

(f) Sodium Acetate

It is used for neutralization of excess HCl in developing bath.

(g) Acetic acid

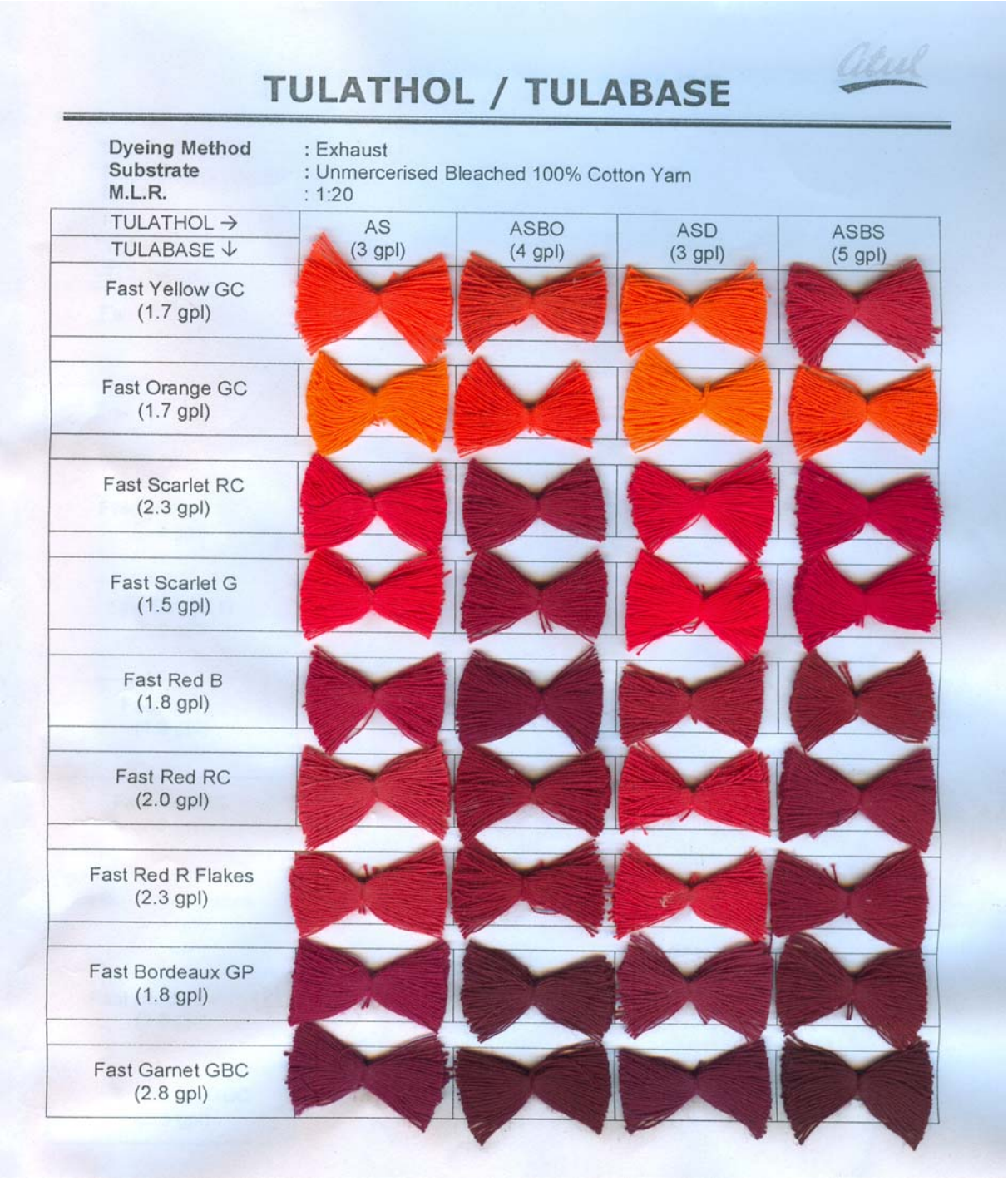
It is used as an alkali binding agent in developing bath.

Stripping of faulty dyeing- a guideline

- Treat the dyed material with 1 g/l non-ionic detergent (TULACHEM Wettex LF) and 3-5 g/l caustic soda near boil for 15 minutes.
- Cool to 85^{o}C.
- Add 3-5% sodium hydrosulphite. Run for 30-45 minutes at 85^{o}C.
- Hot rinse
- Cold rinse
- Bleach with 1-2 g/l (available chlorine) for 20 minutes.
- Antichlor and neutralise.
- Soap near boil for 15-20 minutes
- Hot rinse
- Cold rinse
- Dry

TULATHOL / TULABASE – Various shades

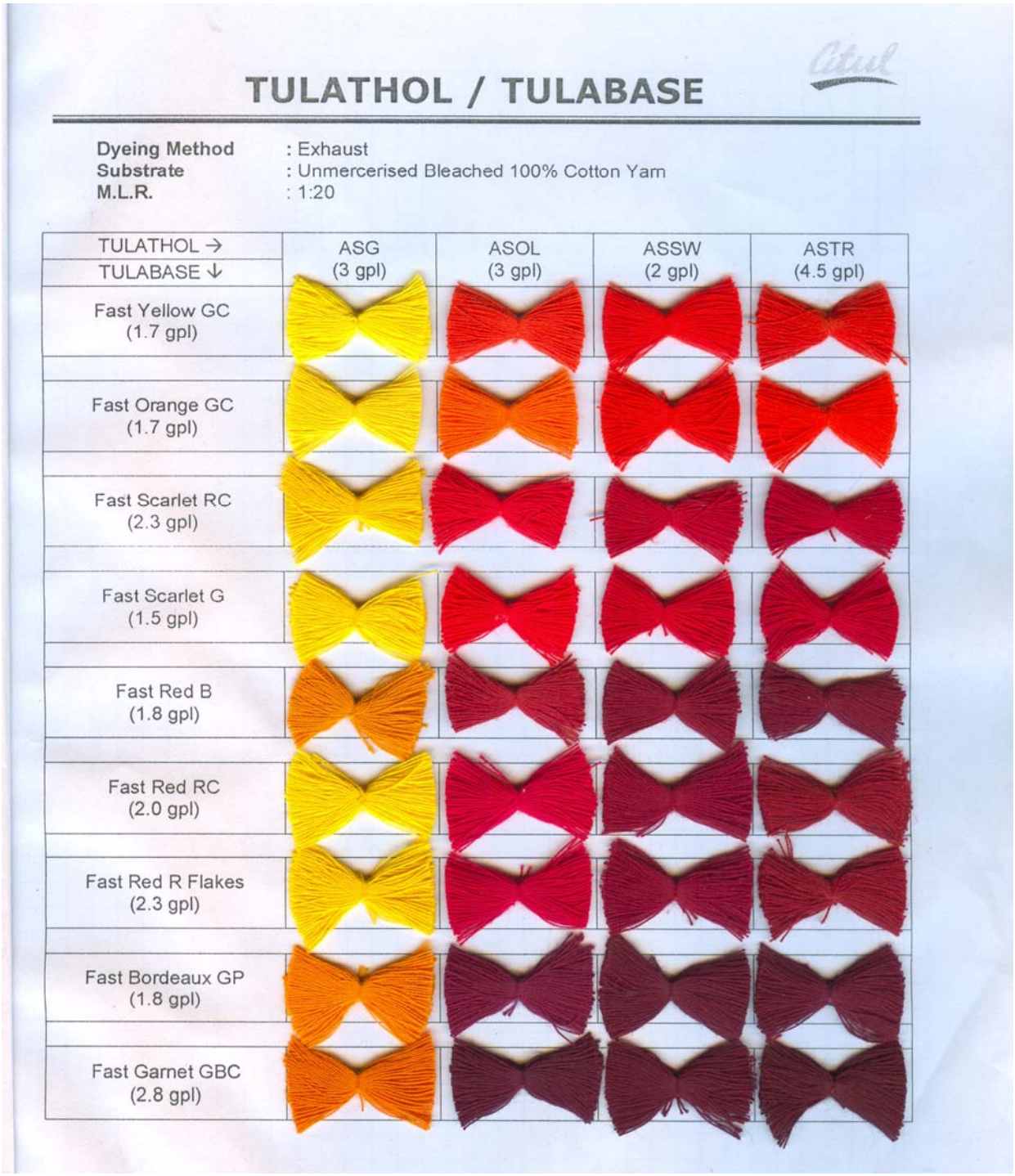
TULATHOLS in combination with different TULABASES can give a very large number of different shades. Widely used shades, produced by TULATHOLS / TULABASES are furnished below:



TULATHOL / TULABASE

Dyeing Method : Exhaust
Substrate : Unmercerised Bleached 100% Cotton Yarn
M.L.R. : 1:20

TULATHOL → / TULABASE ↓	ASG (3 gpl)	ASOL (3 gpl)	ASSW (2 gpl)	ASTR (4.5 gpl)
Fast Yellow GC (1.7 gpl)				
Fast Orange GC (1.7 gpl)				
Fast Scarlet RC (2.3 gpl)				
Fast Scarlet G (1.5 gpl)				
Fast Red B (1.8 gpl)				
Fast Red RC (2.0 gpl)				
Fast Red R Flakes (2.3 gpl)				
Fast Bordeaux GP (1.8 gpl)				
Fast Garnet GBC (2.8 gpl)				



Globally, there has been a paradigm shift in the Concepts and Technology of dyeing. Consumer expectations regarding requirement of reliable results satisfying very stringent fastness properties, quality products, reduced lead-time for delivery, etc. are increasing day by day.

Importance of age old technique of azoic dyeing on cellulose has gradually reduced due to the complex application process, limited gamut of shades and toxic nature of chemicals used. But, still today, azoic dyeing remains green in dyer's mind due to production of very deep and bright shades, energy conservation, good light / bleach / wash fastness properties, absence of photo-degradation problem, suitability in tie-dye / space dyeing and cost economies. Depending on the type of the equipment available, different Naphthol / Base dyeing methods are practiced by dyers, e.g. open beck, tub-dip, circulating liquor, jigger, padding methods, etc. These involve use of different material to liquor ratio and therefore different concentrations of the dyestuffs are used to get the same shade.

The fastness to washing of azoic combination dyeing on cotton is usually very good to excellent, but only after careful elimination of particles of azo pigment loosely adhering to exposed fibre surfaces. Intermediate drying or rinsing of fabric containing the Naphthol, and the thorough soaping of the final dyeing, are key processes ensuring optimum desired fastness. Also, for achieving optimum rubbing fastness, deep dyeing should be thoroughly soaped, otherwise they easily transfer colour onto adjacent white fabric, even under conditions of gentle rubbing. Though normally, azoic dyeings offer good light and chlorine bleach fastness properties; but in case of some pale shades (particularly under humid conditions), much reduced light fastness is obtained and some sensitive azoic combinations also give dyeings of only fair resistance to chlorine bleaching. Sometimes, for achieving improved fastness properties, topping of azoic shades with vat dyes are practiced.

Since many years, with the TULATHOL / TULABASE range, Atul Ltd. continues to cater the need of dyers, by offering a wide range of cost effective high performance deep and bright colours with desired shade gamut. These products are manufactured satisfying strictest quality control parameters and environmental norms and TULATHOL / TULABASE range is poised to provide total azoic dyeing solutions to our esteemed customers.