Classifications, properties and applications of textile dyes: A review

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Abstract

A review of the literature on the chemical structure of the textile dyes. This review discusses characteristics associated with the production and use of textile dyes throughout the world. In addition, the data discussed mainly concerns the in terms of their chemical structure (Azo dyes, Nitro dyes, Indigo dyes, Anthraquinone dyes, Phthalein dyes, Triphenyl methyl dyes, Nitrated dyes) and application of these dyes in the textile industry.

Keywords: Chemical structure of the textile dye and use of textile dyes.

1. Introduction

The first known use of an organic colorant was much later, c. 4000 years ago, when the blue dye indigo was found in the wrappings of mummies in Egyptian tombs[1].

There are more than 100,000 commercially available dyes with over 7 107 tons of dyestuff produced annually worldwide[2]. These dyes are widely used in a number of industries, such as textiles, food, cosmetics and paper printing, with the textile industry the largest consumer of dyes[2].

The textile industries now predominantly use synthetic organic dyes like direct dyes, processing dyes, reactive dyes, etc. The large variety of dyes and chemicals used in an attempt to make more attractive popular shades of fabrics for a competitive market render them very complex. During the last decade, environmental issues associated with dyestuff production and application have grown significantly and are indisputably among the major driving forces affecting the textile dye industry today[3].

The word ‘natural dye’ covers all the dyes derived from the natural sources like plants, animal and minerals. Natural dyes are mostly non-substantive and must be applied on textiles by the help of mordants, usually a metallic salt, having an affinity for both the colouring matter and the fibre[4].

Synthetic dyes are extensively used in wide range of industries amongst which textile processing industries are the major consumers[5].

Perkin was the pioneer in producing man made organic dye, mauve, as early as 1856. The first synthetic organic dye was produced in 1871 when Woulfe prepared picric acid by treating the natural dye, indigo with nitric acid. Since then several new chemical dyes have been added to the everincreasing list of dyes[3].
The textile industry accounts for the largest consumption of dyestuffs at nearly 70 percent. Reactive Dyes, Vat Dyes and Azo Dyes are mainly required for dyeing and printing of cotton fibers[6]. Disperse dyes constitute the largest market with about 21% share followed by direct dyes and reactive dyes with 16% and 11% respectively. Textile dyes are generally classified either in accordance with their chemical constitution or their application to textile fibers and other coloring applications[6]. The main purpose of this review is to critically discuss the recent developments textiles dyes chemistry and their applications in dyeing textiles.

2. Textile dyes used in dyeing and printing industries

Textile dyes have been classified according to their chemical structural (Azo dyes, Nitro dyes, Indigo dyes, Anthraquinone dyes, Phthaline dyes, Triphenyl methyl dyes, Nitrated dyes, etc.) or their industrial application. Table 1 presents the classification of textile dyes according to their chromophore.

Table 1. Classification and examples of dyes according to the chromophore present[7].

<table>
<thead>
<tr>
<th>Class</th>
<th>Chromophore</th>
<th>Exemple</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azo dyes</td>
<td>( \text{-N=N-} )</td>
<td>Acid Red 337</td>
</tr>
<tr>
<td></td>
<td><img src="image1" alt="Azo dye structure" /></td>
<td></td>
</tr>
<tr>
<td>Nitro dyes</td>
<td>( \text{-NO}_2 )</td>
<td>Disperse yellow 14</td>
</tr>
<tr>
<td></td>
<td><img src="image2" alt="Nitro dye structure" /></td>
<td></td>
</tr>
<tr>
<td>Indigoid dyes</td>
<td><img src="image3" alt="Indigoid dye structure" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C.I. Vat Blue 35</td>
<td></td>
</tr>
</tbody>
</table>
Anthraquinone dyes

Phthalein dyes

Triphenyl methyl dyes

Nitroso dyes

Fluorescent-labeled nitroso compound (DNSBA-NO) were synthesized by methods[8].
2.1. Azoic dyes

According to Masoom et al.,[9] have been confirmed to, the yearly world production of azo dyes is assessed to be about 1 million tons. It is found in diverse forms and natures and more than 2,000 fundamentally different azo dyes are presently in use. Azo bond linkage (–N=N–) may be present more than once, mono azo dyes have one azo linkage. While, there are two linkages in diazo dyes and three in triazodyes respectively.

According to Lucas et al.,[10] and other[11] have been reported to Azo dyes are the largest class of synthetic dyes. Approximately 70% of all the dyes used in industry are azo dyes. They are widely used in textile, cosmetic, leather, pharmaceutical, paper, paint and food industries.

Sabnis et al.,[12] have been confirmed to, the azo dyes represent the greatest production volume in dyestuff chemistry today, and their relative importance may even grow in the future. The huge success of azo dyes is due to several factors: the simplicity of the coupling reaction, the immense possibilities for structural variations and adaption to the needs of the most diverse applications for these dyes, and the often very high molar extinction of azo compounds.

According to same authors have been reported to, the About 50,000 tons of textile dyes are discharged in the environment annually from dyeing processes globally.

Chang, et al., [13] have been confirmed to, the azo dyes make up about one-half of all dyes synthesized and are predominantly used synthetic dyes in the textile, food, paper, printing, leather and cosmetic industries. Azo dyes have diversity in structure but their most important structural feature is presence of azo linkage i.e., N=N. This linkage may be present more than one time and thus mono azo dyes have one azo linkage while two in diazo and three in triazo, respectively.

According to zollinger et al.,[14] have been reported to, these azo groups are connected on both sides with aromatics like benzene and naphthalene moiety. Sometimes aromatic heterocyclic units are also present being connected with azo groups.

McMullan et al.,[15] have been demonstrated to, the different shades of the same dye having various intensities of color are due to these aromatic side groups[16].

According to Rajaguru et al.,[17] have been reported to, the azo dyes containing sulfonate groups as substituent are called as sulphonated azo dyes. Azo groups in conjugation with aromatic substituents or enolizable groups make a complex structure which lead to huge expression of variation of colors in dyes. Example of azo dyes is shown in Fig. 1 following.

![Figure 1. Example azo dye](image-url)
2.2. Reactive dyes

They make it possible to obtain a high wet strength (better than the less expensive direct dyes), but their use is not always possible because of difficulty in obtaining good unison. The chlorine-fastness is slightly lower than that of the vat dyes, as is the light fastness under extreme conditions.

Farouk et al.,[18] and others have been reported to, the reactive dyes are the only textile colourants designed to form covalent bond with the substrate during the application process, reactive dyes furnish a wide gamut of shades of good light fastness and excellent wash fastness on cotton. Such properties place this class of dyes at the quality end of the market.

According to Gao et al.,[19] and authors[20] have been reported to, the reactive dyes used for cellulose are reactive and an increasing amount is used on wool and nylon.

According to Jiraratananon[21] et al., and others[22] have been confirmed to, the poor dye fixation has been a longstanding problem with reactive dyes.

The first commercial reactive dyes for cotton were based on the dichloro-s-triazine reactive group. Since then many other reactive groups have been developed[23] [24] [25] [26]. The example of reactive dyes is shown in Fig. 2 following.

![Figure 2. Dye (C.I. Reactive Red 198).](image)

2.3. Vat dyes

According to Burkinshaw et al.,[27] have been reported to, the vat dyes are intended for application to cellulosic fibres, notably cotton, on which they characteristically display unparalleled levels of fastness to a variety of agencies (e.g. washing, bleach, light, etc.), this being attributable, in the most part, to their water insolubility. Vat dyes enjoy little, if any, usage on other types of fibre, for which alternative dye classes are instead preferred; indeed, in the context of synthetic fibres, the typically low substantivity displayed by vat dyes coupled with the generally pale depths of shades that arise from their limited diffusional behaviour within the fibres, results in them being very little used on such substrates.

According to Preston[28] has been reported to, the derivatives of indigo, mostly halogenated (especially bromo substituents) provide other vat dye classes including: indigoid and thiindigoid, anthraquinone (indanthrone, flavanthrone, pyranthone, acylaminoanthraquinone, anthrimide, dibenzanthrone and carbazole).
The most important natural vat dye is Indigo or indicotin found as its glucoside, indican, in various species of the indigo plant indigofera. Vat dyes are used where very high light- and wet-fastness properties are required. The typical chemical structures of vat dyes are given in Fig. 3.

![Vat Blue 5]

![Acid Blue 74]

**Figure 3.** Chemical structures of vat dyes.

### 2.4. Sulphur dyes

According to Nguyen et al.,[29] have been reported to, in 1966, sulfur dyes represented 9.1% of total US dye production and 15.8% of the dyes made for use on cellulosic fibers, and the world production was estimated at 110,000–120,000 tons per year. Shankarling et al.,[30] have been reported to, this is the highest production percentage of any group of dyes. In 2007, sulfur dyes were the third-highest produced dyes in China at 8500 tons. Wang et al.,[31] have been confirmed to, half of the volume of all dyes used on cellulosic fibers are sulfur dyes37, of which approximately 80% are black sulfur dyes. Sulfur dyes with a constitution number are defined in the Color Index 53185, 53228, 53810, etc. by the starting materials and the type of sulfurization[32].

Sulfurization involves various reactions, including substitution, ring formation, reduction, and oxidation. The starting materials generally include relatively common aromatic compounds, including benzene, naphthalene, diphenyl, diphenylamine, azobenzene, etc., which bear at least one nitro, nitroso, amino, substituted amino, or hydroxy group. Sulfur dyes are mainly used for dyeing textile cellulosic materials or blends of cellulosic fibers with synthetic fibers[33], but they also find specific applications in the dyeing of silk and paper in limited quantities and use on certain types of leathers. Amongst synthetic dyes, sulfur dyes have the dullest range of colors of all dyestuff classes, are inexpensive and exhibit excellent washing and good light fastness. These properties, along with the ease of application, ensure that the consumption of sulfur dyes remains high. Fig. 4 illustrates some reported four sulfur dyes in the literature.
Sulphur dyes are used for dyeing deep muted shades and offer good wetfastness and moderate to good light-fastness. These dyes are very complex in structure and for the main part are unknown; the majority are prepared by thionation of various aromatic intermediates. The first commercial sulphur dye marketed as Cachou de Laval (C.I. Sulphur Brown 1)[34] was prepared by Croissant and Bretonnière in 1873 by heating organic refuse with sodium sulphide or polysulphide. However Vidal obtained the first dye in this class from intermediates of known structure in 1893[33].

2.5. Acid dyes

According to Nunn[35] has been reported to, these dyes can be applied to nylon, wool or silk in the pH range 3.0–7.0. The wet-fastness of these dyes varies from moderate to good and their lightfastness is generally in the blue-scale range 5.0–6.0.

The dyes are generally applied under acidic conditions (using formic or acetic acid) with the degree of acidity depending upon individual dye properties. Acid dyes are generally bright with a variable fastness to washing. Structurally the dye molecules vary greatly and include some metal complexes. The defining feature of the group is the presence of sulphonated groups, these provide water-solubility. Bonding to wool occurs partially due to interaction between these sulphonate groups and ammonium groups on the wool fibre. Additional bonding interaction is provided by Van der Waals forces. The degree of interaction, and hence, the degree of colour fastness varies directly with dye molecule size.

Acid dyes are azo chromophoric systems (the most important group), anthraquinone, triphenylmethane or copper phthalocyanine, which are soluble in water by the introduction of one to four sulphonate groups. The example of these dyes are shown in Fig. 5
2.6. Disperse dyes

According to Hunger et al., [32] have been reported to, the disperse dyes are synthetic colorants for hydrophobic substrates and are commonly applied as commercial mixtures in textile coloration. They are often used in great quantities and due to the huge amount of water involved in the associated dyeing processes and the high proportion of the dye that remains in the water bath, large volumes of wastewater can be generated.

Broadben et al., [36] have been confirmed to, these dyes are frequently insoluble or sparingly soluble in water, non-ionic in character and applied to hydrophobic fibres from an aqueous dispersion. They are predominantly used on polyester but have found application to nylon, cellulose acetate and acrylic fibres, although some of the wet-fastness properties of the dyes on these substrates are poor. The dyed substrate is usually given a reduction clear following dyeing, in order to clean the substrate surface of dye that would cause staining if left untreated. These dyes were traditionally applied to polyester at the boil with the inclusion of a carrier in the dyebath to facilitate diffusion of the dye into the substrate. A typical disperse dye structure is shown in Fig. 6

![Disperse Red 8](image)

**Figure 6.** Chemical structure of C.I. Disperse Red 8

2.7. Basic dyes

According to Broadben has been reported to, these dyes are usually applied to acrylic, paper and nylon substrates, but can also find use in some modified polyester substrates. Basic dyes are often applied with retarders due to their poor migration properties at the boil. This poor migration is due to the high substantivity of the dye for the substrate and rapid increase in diffusion at high temperatures. Basic dyes are water-soluble and produce coloured cations in solution; these cations are attracted electrostatically to substrates with a negative charge. Basic or cationic dyes can have either the positive charge localised on an ammonium group (these dyes are characterised by a high tinctorial strength), or it can be distributed as a delocalised charge over the dye cation as found in many triarylmethane, xanthenes and acridine dyes. Example of the basic dye is given in Fig. 7

![Basic Blue 22](image)

**Figure 7.** Basic Blue 22
2.8. Direct dyes

According to Burkinshaw et al., [37,38] have been reported to, the direct dyes are classified according to many parameters such as chromophore, fastness properties or application characteristics. The major chromophoric types are as follows: azo, stilbene, phthalocyanine, dioxazine and other smaller chemical classes such as formazan, anthraquinone, quinolone and thiazole. Although these dyes are easy to apply and have a wide shade gamut, their wash-fastness performance is only moderate; this has led to their replacement somewhat by reactive dyes which have much higher wet and washing fastness properties on cellulosic substrates. Example of the basic dye is given in Fig.8

![Figure 8. C.I. Direct Red 2](image)

3. Conclusion

Hence this review presents gives the classification of dyes by dye class, their applications, Principles, follow the preparation of substrates for dyeing and the thermodynamics of dyeing systems. Each dye class is described in detail giving more specific information regarding the chemistry of the dye class and the most common mode of application.

References

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