Chapter 3: Vat Dyes and Their Application

By J. R. ASPLAND, School of Textiles, Clemson University, Clemson, S. C.

Long before the advent of systematic physical sciences and the growth of the chemical industry, as long as 5000 years ago in India, dyeing methods were being used for the application of the water insoluble pigment, indigo, to natural fibers. In the early nineteenth century, between the first cotton gin and the Civil War, the value of natural indigo produced in South Carolina exceeded that of rice or cotton.

Indigo was first recovered from the water soluble glucoside of indoxyl (indican) present in the plants *Indigofera* and *Isatis tinctoria*, and then the insoluble blue product was dissolved in wooden vats by a natural fermentation process later known as *vatting*. This was the origin of the name *vat* dyes. Chemically speaking, vatting is a reduction.
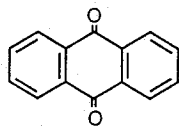
In the right conditions, the known animal and vegetable (cellulosic) fibers accepted the greenish-yellow material dissolved in the vat, and on subsequent exposure of the dyed fibers to the oxygen in the air, the color was converted back to that of the original indigo pigment. Restoration of the indigo is an oxidation. Both oxidation and reduction will be discussed

1a) Anthraquinone

1b) Indigo

Fig. 1. Parent chemicals of most vat dyes.

after the section on functional groups in vat dyes.

Another natural vat dye, a brominated derivative of indigo, was derived from the shellfish *Murex brandaris*, found in small quantities at the eastern end of the Mediterranean. It was known as Tyrian Purple and was once important for its rarity and its hue. The Roman emperors practically monopolized it, which gave rise to the term royal purple.

Since the massive growth of indigo dyed denim, beginning in the 1970s, indigo is one of the most important single dyes in use today. However, little natural indigo is produced now, for chemical synthesis gives a much more consistent and economical product. Synthetic indigo was first marketed in 1897.

In some ways, despite its long history and current importance, it is almost unfortunate that indigo must be classified as a vat dye, because the present application methods for indigo and the fastness properties of indigo dyeings are not typical of vat dyes as a whole. Since the discovery of indanthrone (now C.I. Vat Blue 4) by R. Bohn in 1901, many vat dyes with no natural equivalents have been synthesized. Dyeings of the products which have survived in the marketplace normally show outstanding colorfastness properties, particularly to light, washing and chlorine bleaching, while indigo dyeings have poor resistance to most of these and poor abrasion resistance as well.

The majority of vat dyes in use today are, like Vat Blue 4, derivatives of anthraquinone. Exceptions are C.I. Vat Reds

1 and 41 *(1)*. Fig. 1 shows the structure of both anthraquinone and indigo *(2)*. The present importance of the indifferent dye, indigo, should teach a salutary lesson in marketing. Satisfying the needs of the customer is generally more important than achieving the highest levels of technical performance in dyed and finished goods, although the two sometimes coincide. Since the early 70s, customers have wanted indigo blue denim primarily for the appearance which can result from the inferior fastness properties of the dyeings. This is exploited by garment dyers and finishers in stonewashing and other wet processes.

Let us now look at the general nature of vat dyes and vat dyeing so that the reasons for the vat dyeing processes in use today can be understood.

General Nature of Vat Dyes

Vat dyes are sold as water insoluble pigments, so why are they called dyes? Like all other dyes, under the right circumstances, they can:

● Be dissolved to give solutions containing individual molecules or molecular ions,

● Be transported to the surface of the fiber and

● Be sorped on and diffuse into suitable fiber.

Note: Steps 1 and 2 are not necessarily placed in this order in dyeing processes.

Vat pigments need alkaline reduction to dissolve them, and they are treated to an additional step (oxidation), which causes the original insoluble pigments to be regenerated, once the soluble ions have diffused within the fiber. Nevertheless, the third step, the sorption and diffusion of suitable derivatives of vat dyes into cellulosics, parallels that of direct dyes quite closely.

One of the keys to successful dyeing with vat dyes is to have control over how and when to convert the pigmentary colors into water soluble coloring chemicals, under conditions in which they will diffuse uniformly into the fibers.

Functional Groups

In the insoluble pigmentary form, all vat dyes have a common chemical feature. They all contain one or more pairs of carbon atoms, all of which are doubly bonded to an oxygen atom. These carbon
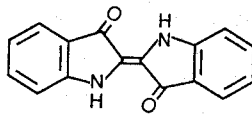
ABSTRACT

Part 1 of this chapter covers the chemical development of vat dyes and the general principles of their application to cotton. The first vat dye discovered (and now the most popular, indigo) does not exhibit the superior fastness properties or follow the application methods typical of most other dyes in its class. Vat pigments, dissolved as leuco-vat dye anions, follow the general model for dye anion sorption and diffusion presented in Chapter 1. Practical dyeing principles of vat dyes will be discussed in Part 2 of this chapter to be published next month.

KEY TERMS

Dyes
Dyeing
Functional Groups
Indigo
Leuco-Vat Anions
Oxidizing Agents
Pigments
Reducing Agents
Vat Dyes

atoms are always part of a condensed system of benzene or other aromatic ring structures (which look like chicken wire when drawn) with a closed system of alternating double and single bonds between adjacent carbon atoms. Since carbon is involved with four chemical bonds, these carbon-oxygen structures can be drawn in the manner shown in Table Ia or Fig. 2a. The same features are shown in Fig. 1. Fig. 2 shows the structures of the functional groups of vat dyes cut to the bone. For simplicity, Fig. 2 only shows one of each functional group; but remember, these are present in pairs in vat colors. As is usual in organic chemistry, where the lines representing chemical bonds intersect, there are carbon atoms. Also shown in Fig. 2 are the reactions of the functional groups necessary for dyeing (See the second portion of this chapter titled Practical Dyeing.)

The structure shown in Fig. 2b is derived from the vat pigment functional group shown in Fig. 2a and is indicative of the water soluble sodium salt known as the sodium leuco-vat dye. In strongly alkaline solutions (pH 12-15), the sodium salt of the leuco-vat dye is fully ionized to give a negatively charged dye anion with associated positively charged sodium cations. Under acidic conditions, this may be converted to the insoluble or sparingly water soluble vat-acid form of the vat dye, Fig. 2c.

The reversibility of the reactions shown in Fig. 2 are denoted by the double arrows which point in opposite directions.

The leuco-vat anion may be compared with water soluble direct dye anions, for it is the anion which is responsible for vat dyeing. Incidentally, the word *leuco* comes from the Greek word *leucos*, meaning white, for this is the color of the vat-acid of indigo.

Table I lists some functional chemical features of vat dyes and their derivatives, along with the names of the compounds and some of their characteristic properties. The corresponding colors are shown for C.I. Vat Blue 1 and Green 1. Such marked color differences between vat-pigment, sodium leuco-vat and vat-acid are not unusual and can give a dyer some visual help in assessing the chemical conditions in the dyebath.
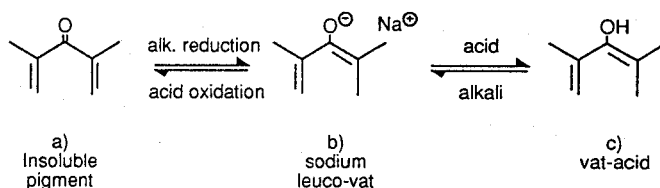

Fig. 2. Vat dye functional groups and their dyeing reactions.

To understand what is happening when vat pigments are dissolved, or the nature and purpose of the aftertreatment of vat dyeings with chemicals, requires at minimum a rudimentary knowledge of what is meant by the terms reducing agents, reduction, reduction potential, oxidizing agents, oxidation and oxidation potential. Chemical systems which incorporate both reduction and oxidation reactions are known as redox systems.

Reducing Agents

Reducing agents are compounds which either donate hydrogen to, subtract oxygen from or add electrons (negative charges) to other chemicals. The affected chemicals are said to be reduced. During the reduction process, the reducing agent itself is changed (oxidized), often irreversibly. For example, the vat pigment structure in Fig. 2a is reduced to give the structures shown in Fig. 2b the soluble sodium leuco-vat, or 2c the sparingly soluble leuco vat-acid, which have an added negative charge and a hydrogen atom respectively.

In vat dyeing, the reducing agent of choice is sodium hydrosulfite, commonly known as hydro but more correctly known as sodium dithionite, which has the chemical formula $Na_2S_2O_4$. This compound is not stable in neutral or acid solution but is stable in strongly alkaline solutions in the absence of air. Unfortunately, oxygen in the air does react with hydro to give sodium sulfite and sodium sulfate, Na_2SO_3 and Na_2SO_4.

To be practically useful, solutions of a vat dye reducing agent must have a level of reducing power (reduction potential) sufficient to reduce all commercial vat dyes to their water soluble forms, economically and quickly, without converting the dyes to products from which the original pigments cannot be restored (over reduction).

Alkaline solutions of hydro generally meet these requirements, although some of the hydro is used up in the process and more is destroyed by its reaction with oxygen in the air (oxidation) especially at higher temperatures. Since the hydro degradation products can be acidic, and are neutralized by the alkali, the alkali is also used up during the process. Consequently, enough alkali must be present initially to insure that the bath remains strongly alkaline and reasonably stable throughout any desired dyeing process. This strong alkalinity is one of the factors which effectively limit the application of conventional vat dyes to the alkali-insensitive cellulosic fibers, although in special cases it is possible to dye other fibers with vat dyes.

Various reducing systems for vat dyes have been proposed and used but alkaline hydrosulfite generally has proved to be the most satisfactory. These include thiourea dioxide, which is relatively expensive and can over-reduce some dyes, and several hydroxyalkylsulfinates used selectively for printing and high temperature applications.

The stability of the alkaline solutions of reducing agent decreases with increased temperature, increased surface exposed to the air, increased agitation of the bath and decreased concentration.

Oxidizing Agents

Oxidizing agents are compounds which either add oxygen to, subtract hydrogen from, or take electrons away from other chemical compounds. The overall effect may be either the loss of negative charge or the gain of a positive charge. Such reactions are called oxidations. Oxidation is essentially the opposite of reduction. In the course of oxidizing any chemical, the oxidizing agent is reduced. Conversely, in the course of reducing any chemical, the reducing agent is oxidized. Oxidizing and reducing agents can be seen to go hand in hand, much like acids and bases, positive and negative, male and female. When the structure given in Fig. 2b is treated with an oxidizing agent, it loses an electron from the anion and reverts to the original pigmentary form with the double bonded oxygen, Fig. 2a. Similarly, 2c on oxidation is also restored to 2a, this time with the loss of a hydrogen.

To convert fibers dyed with sodium

Table I. Chemical Features and Selected Properties of Vat Dye Derivatives

Chemical Structures	Compound Name and Form	Water Solubility	Cellulose Substantivity	C.I. Vat Name Blue 1 (Indigo)	Green 1
a) $C = O$	vat pigment	none	none	indigo blue	jade green
b) $C-O^-$ Na^+	sodium leuco vat (anionic vat dye)	soluble	substantive	yellow	blue
c) $C-OH$	leuco compound (vat acid)	sparing	none	white	red

Vat Dyes

leuco-vats back to fibers containing imbedded vat pigments, the oxidizing agent is frequently an aqueous solution of a per-compound such as sodium per borate or hydrogen peroxide in the presence of acetic acid, which will also help to neutralize any alkali present in the residual reducing solution. It is important for any acid treatment not to precede but to be concurrent with the oxidation. As shown in Fig. 2, it is possible, but undesirable, to form sparingly soluble vat-acids at this late stage of a vat dyeing process, for they oxidize quite slowly.

For some vat dyes, in some circumstances, the oxidation potential of hydrogen peroxide solutions is too great and over-oxidation—i.e., beyond the oxidation state of the original pigmentary form of the dye—can take place. In these circumstances, a compound known chemically as the sodium salt of metanitrobenzenesulfonic acid is used as a much milder but more expensive alternative oxidizing agent, and this operates well in alkaline conditions. The oxygen in the air is an adequate oxidizing agent for returning the reduced form of vat dyes to the original pigmentary form, but clearly, in practical circumstances, where it is necessary to oxidize the goods rapidly and uniformly, one cannot always afford to wait for the relatively slow action of the air upon the goods, particularly when the goods are in the form of compact structures such as raw stock cakes, cloth on beams and yarn packages.

In general one can say that vat dyes are relatively difficult to reduce but relatively easy to oxidize. This contrasts nicely with the sulfur dyes which are just the reverse—easy to reduce but more difficult to oxidize.

Soaping

After sodium leuco-vat anions have diffused into cellulosic fibers, after the excess alkali and reducing agents have been washed-off, after the oxidation has been accomplished and the pigmentary form of the vat dye is left imbedded within the cellulosic fibers, then comes soaping.

Soaping is peculiar to vat dyes and it is misnomer in that it does not require the use of soap. It can describe any treatment, in near boiling aqueous solutions containing a surfactant, during which the isolated molecules of vat pigments are reorientated and associate into a different, more crystalline form. This new form can have a significantly different shade and gives the dyed goods materially improved fastness to light and washing. Unfortunately, on continuous dye ranges, there is rarely enough time to complete a soaping process. Vat dyes which undergo minimal

shade change on soaping may have to be used.

Leuco-Vat Dye Anions In Solution

The physical principles treated at some length in Chapter 1, in the section titled Dye-Anions: Solution, Sorption and Diffusion, are as applicable to leuco-vat dye anions as they are to any of the other application classes of anionic materials for cellulosic fibers. But there are some points still worth reviewing.

Solution and Sorption

Relatively large amounts of alkali and reducing agent, both sources of sodium ions, are necessary to dissolve the vat pigment. Because of this, the sodium ion content and the chemical potential of leuco-vat dyes in solution start from a high baseline. For many dyes there is no need of additional common salt to insure that the surface negative potential of the fibers is overcome and that dye sorption can take place rapidly. In other words, the high substantivity of leuco-vat anions is largely due to the high salt content of their solutions.

But there is a range of substantivities and solubilities which is largely dependent upon the individual molecular structure of the different dyes. Like direct dyes, some of the vat dye molecules are linear, some are planar and some are both. These factors encourage dye aggregation at the fiber surface. Indigo dyeing depends on this surface dye aggregation.

Kinetics of Sorption

The sorption of the dye anions at or near to the fiber surfaces, shown in Chapter 1, Fig. 3a, is so relatively rapid for leuco-vat dye anions that this stage of dyeing may be considered as separate and distinct from the much slower process of gradual diffusion of the anions inside the fibers (3). So much so, that 80-90% of the color can be exhausted onto the fiber surfaces within the first ten minutes of dyeing. *Note*: The dyeing rate constant, k_{dye}, and the stripping or leveling rate constant, k_{strip}, both increase with increasing temperature.

Batch dyeing procedures are tailored to take this into account.

Freundlich Sorption Isotherms

Like other anionic dyes on the nonionic cellulosic fibers, the vat dye-anion sorption isotherms are of the Freundlich type, Chapter 1, Fig. 4b). This means that the concentration of dye on the fiber can always be increased by addition of more dye to the dyebath. But, practically speaking, there is a dye concentration above which the color change obtained by further dye addition cannot justify the added cost.

Dyeing Equilibrium

The simple arithmetical model of dyeing presented in Chapter 1 is also applicable to vat dye anions. But remember: the values of constants such as the dyeing rate constant, k_{dye}, the stripping or desorption constant k_{strip}, and the substantivity or partition coefficient, K, are all very dependent upon the prevailing conditions in the bath. These include the salt concentration, the liquor-to-goods ratio, L, and the temperature. The relationship between percentage exhaustion, liquor ratio and partition coefficient, is worth reiterating: $\%E = 100 \ (K/(K+L))$. *Note*: At the end of a dyeing, $\%E$ and K can both be increased with the addition of salt and lowering the temperature. Batch dyeing procedures are also tailored to take this into account.

Review

In 1901, C.I. Vat Blue 4, indanthrone, was synthesized from anthraquinone and spurred the discovery of the whole range of vat dyes, of mostly superior fastness, which are available today. The discovery of hydro (sodium dithionite) in 1904 was equally significant.

Vat dyes are in fact pigments. In alkaline reduction they dissolve in water as the leuco-vat dye anions. These anions have substantivity for cellulosic fibers from the reducing baths and their dyeing properties closely resemble those of the simpler direct dye anions.

Once the leuco-vat anions are within the cellulose, the original pigment is regenerated by removing the reducing system and replacing it by an oxidizing system. This procedure gives vat pigment molecules within the fiber. The fastness properties of the dyeings may be enhanced by soaping, during which individual pigment molecules are rearranged, aggregate and crystallize.   ∞

References

(1) *AATCC Buyer's Guide for the Textile Wet Processing Industry*, AATCC, published annually as the July issue of *Textile Chemist and Colorist*.

(2) *Colour Index*, Society of Dyers and Colourists and AATCC, Vols. 3 and 4, Third Edition, 1971.

(3) *The Dyeing of Cellulosic Fibres*, edited by Clifford Preston, Society of Dyers and Colourists, 1986, Chapter 6.