Chapter 3/Part 2: Practical Application of Vat Dyes

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IN the 1980s vat dyes, bearing about 60 C.I. Names (*1*), were available in the U.S. under about 260 different trade names. This collection of dyes has not changed much in recent years. About 60% of them have C.I. Numbers—i.e., the chemical structure of the principle color component is known; 85% are derivatives of anthraquinone, and of these almost 50% fall into only five chemical structure subgroups; indigo derivatives and the related thioindigo derivatives account for about 10% of the list. As a class, vat dyes are expensive, although they share this characteristic with some fiber reactive dyes. One should not overlook the 10% of so-called sulfurized vat dyes, which are more economical hybrids of sulfur and vat dyes.

ABSTRACT

The practical details of using vat dyes in both batch and continuous processes are covered in this second and final part of Chapter 3. Vat dyes generally offer superior fastness properties. Potential drawbacks to selecting vat dyes include a tendency for phototendering and a limited color gamut. Based on the substantivities of leuco-vat anions, the traditional classification system for vat dyes offers batch dyers a better means for selecting vat dyes to be used successfully in combination. Leuco-vat dyeing, prepigmentation, semi-pigmentation and batch aftertreatments are covered. While continuous dyeing with vats offers economic advantages, several precautions are required to ensure a satisfactory result. The chemical structure and commercial forms of vat dyes are also covered.

KEY TERMS

Anthraquinonoid Vat Dyes
Batch Aftertreatments
Color Gamut
Commercial Form
Continuous Dyeing
Dye Classification
Fastness Properties
Indigo Dyeing
Pigmentation
Vat Dyeing
Wet-on-Wet Process

Vat Dye Classification

The products in all dye application classes may be differentiated in several ways: e.g., by their chemical nature, by the fastness properties of the dyeings (and consequently, their end-uses), by their dyeing characteristics, or even by their color. Because vat dyes are sold as pigments, it is important to be aware that dissolution and other dyeing related properties can be affected by the particle size distribution of the products (*2*).

Vat Dye Synthesis

Vat dyes are difficult chemicals to make and their structures are complex. Some of these will be shown in the subheading Vat Dyes. The different chemical structures affect the solubility of the sodium leuco-vat, its stability towards over-reduction and over-oxidation, its substantivity, its rate of diffusion into and out of the fiber and the ultimate properties of the dyeing. But since these application properties cannot be readily deduced from the dye structures alone, classification by structure will not generally be much help in the dyehouse, although all indanthrones (C.I. Vat Blues 4, 6 and 14) are susceptible to over-reduction and over-oxidation.

Fastness Properties

In exchange for their cost, vat dyes can deliver dyeings with the highest levels of washing and wetfastness properties. Indigo, as mentioned earlier, is atypical in this regard. For staining of adjacent cotton goods and shade changes on washing, vat dyeings are rarely rated less than 4-5 on a scale of 5.

Fastness to industrial laundering with hypochlorite and towards peroxide and hypochlorite bleaching are generally outstanding, as are the fastness properties towards sunlight, weathering and perspiration. Even the paler shades of vat dyeings generally have high lightfastness ratings, in the order of 5-6 on a scale of 8, and 7-8 at heavy depths. For further information on lightfastness testing and rating, see (*3*). It is the limited variability of these ratings, as well as their high values, which distinguishes vat dyeings from direct dyeings. However, some combinations of yellow and blue or green vat dyes do show anomalous behavior in which the blue or green component is lost more readily on exposure to light than expected. This is often referred to as catalytic fading, and is, unfortunately, not very predictable (*4*).

Another occasional problem is phototendering, in which some vat dyes, such as C.I. Vat Orange 2, are partly reduced under the influence of light. In the dark, in the presence of atmospheric oxygen and the cellulose, they are regenerated; but with oxidative tendering of the fiber by peroxides formed as by-products. The author's wife has a pocket handkerchief which once sported a vat-printed pattern of small dogs. The dogs are nearly all gone now, leaving small dog-shaped holes.

Despite some drawbacks, which can be circumvented by proper dye selection, vat dyeings have several good properties which make them very difficult to overlook for dyeing some industrial yarns, terry cloth, industrial work clothing and shirting fabrics. They also are the only class of dyes which does not suffer severe shade changes during the application of topical, cellulose reactive, flame retardant finishes.

Color Characteristics

All surface colors can be characterized in terms of three independent parameters—lightness (or darkness), chroma and hue. Chroma is also called colorfulness, saturation or brightness (or dullness). We will use the word brightness here, even though it is not the ideal synonym for chroma and is not to be confused with lightness. Hue is the property of appearing red, yellow, green or blue or something in between.

The color distribution of vat dyes available in the U.S. is as follows: 25% blue, 18% brown, 14% black (and olive), 11% orange, 10% red, 10% green, 6% violet and 6% yellow. There is a good palette for blue, green and earth tones of very good fastness, with similar dye cost to normal fiber reactive dyes. The range of colors which can be dyed with any one application class of dyes is known as the color gamut, which is a volume of colorspace within which these dyes are useful. The color gamut of vat dyes is restricted by the absence of very bright colors, particularly in the red and turquoise hue areas, and only sulfur dyes and azoic combinations have smaller color gamuts.

Batch Dyeing Characteristics

No single classification of vat dyes by dyeing characteristics has been as useful or as generally accepted as has the classification of direct dyes into groups A, B and C.

One method of classification divides vat dyes into four principle sub-groups: IK, IW, IN and IN Special, which still leaves a few dyes out, such as C.I. Vat Black 9. This classification is based on the different substantivities of the leuco-vat dye anions and the corresponding differences in dyeing temperatures and the salt, caustic soda and hydro concentrations necessary to give the best overall dyeing results. The importance of these traditional groupings is restricted to batch dyeing with the leuco-vat anions.

The I stands for Indanthren, and has been a trademark for vat dyes since the synthesis of indanthrone. In the first three decades of the twentieth century, thanks to unusual Anglo-German co-operation between Morton-Sundour Fabrics and BASF, the name Indanthren rapidly became synonymous with outstanding light- and wetfastness on cellulosic fibers.

K stands for the German word, kalt, meaning cold. Dyes (reduced leuco-vat anions) in this group are dyed at room temperature with a relatively high salt concentration (common salt or anhydrous sodium sulfate) and a relatively low sodium hydroxide (caustic soda) concentration, all of which tend to promote higher substantivity and exhaustion at equilibrium.

W stands for the German/English word, warm. Dyes in this group are more substantive, and can be dyed at 40-50C (100-120F) with less salt and slightly more alkali.

N stands for the German/English word, normal. Such dyes are even more substantive, require more alkali but no salt, and can be dyed at 60C (140F). The IN Special dyes require even more alkali.

Table I shows the conditions under which 2% owg shades can be dyed at 10:1 liquor-to-goods ratio for IK, IN and IW dyes. The concentrations of chemicals increase with increasing dye concentrations and liquor-to-goods ratios. For more details a reputable dye supplier should be consulted, since different dye organizations use different methods of categorization (*5*). Also, read carefully the units in which concentrations are expressed. Conveniently, few of the vat dyes in use today fall outside the IW and IN categories. When it is necessary to dye mixtures of IW and IN dyes, the IN conditions are to be selected because the higher temperature and lower salt are least likely to cause unlevelness due to too rapid dyeing.

Batch Dyeing Processes

There are at least two distinct types of vat dyeing processes which will be discussed here. They may be characterized as leuco and prepigmentation methods, and there are also dyeing methods which are hybrids. But before we proceed to look at the different processes in turn, it would be desirable to reiterate a caution, given earlier, regarding preparation and water quality.

Table I. Conditions for Dyeing Leuco-Vat Anions at 10:1 Liquor-to-Goods Ratio

Dye Group	Temperature C (F)	Caustic Soda (g/L)	Hydro (g/L)	Sodium Sulfate (g/L)
IK	20-25 (70-80)	3.6	3.0	12.0
IW	40-50 (100-120)	4.8	4.0	12.0
IN	60 (140)	8.8	5.0	—

Preparation and Water Quality

When dyeing cotton with water soluble anions under conditions of high substantivity, as is the case with leuco-vat anions, it is imperative to have the goods as free as possible from any impurities which might be distributed nonuniformly and which are hydrophobic (e.g., oils, fats and waxes), or which can interact with the dye anions to give hydrophobic (insoluble) products; e.g., the calcium and magnesium cations present in process water and in the cotton itself, from the irrigation water. Anything which might stand in the way of uniformly wetting the goods with dye solution could cause unlevel dyeing. The better the preparation, the more uniform the dyeing. Careful preparation may not put money in the bank, but it could stop second quality goods from eating away assets. The use of sequestering (chelating) agents or protective colloids which complex with calcium and magnesium ions is recommended. Oxidative bleaching pretreatments along with the use of strong alkalis, dispersing agents and sequestering agents often precede dyeing; but it is possible with vat dyes to take advantage of the highly alkaline dyebaths and both prepare and dye greige goods at the same time.

Dye Anion Solubility

The solubility of the sodium leuco-derivatives of vat dyes varies considerably with structure, with some higher than 80 grams per liter and some lower than 15 grams per liter. The C.I. Vat Blues 4, 6 and 14, based on indanthrone, have a tendency both to lose solubility on standing and, along with several others, to form insoluble salts of calcium, magnesium or iron in hard water. As mentioned earlier, a sequestering agent can alleviate this latter problem. At higher temperatures, these same indanthrones are also subject to over-reduction, and C.I. Vat Blue 6 can lose its chloro groups. Additions of glucose or sodium nitrite may help eliminate over reduction.

Leuco-Vat Dyeing

The earliest and the most fundamental vat dyeing process is the leuco-process in which the practical dyeing does not begin until the vat-pigment is dissolved in caustic soda and hydrosulfite solution. Here we have a classical case of anions in solution, their sorption and diffusion into the nonionic cellulosic fiber.

This type of dyeing process is applicable to cellulosic fibers from raw stock through sliver, yarn packages and yarn skeins, to knit or woven fabrics where liquor-to-goods ratios of 10:1 to 20:1 would be in the normal range. Its primary use is for heavy shades, which exhaust less rapidly (see subheading in Chapter 1 titled Kinetics: Rate of Dyeing) and for which the possibility of unlevelness is not so critical. The variety of machinery possible for dyeing fiber in all these forms makes any suggestion of a single optimal procedure absurd. But the variables which affect the levelness or uniformity on the one hand and the dyeing efficiency or exhaustion on the other are well understood. Careful consideration of these variables can be used to effect process optimization in any particular case.

- Temperature: The temperature at the start of the dyeing is determined by the classification of the dye used (see Table I). Vatting is normally carried out prior to dyeing for about 10 minutes in a long liquor. During the dyeing the temperature can be gradually raised to about 80C (170-180F), or even higher if the dyes are not sensitive to over-reduction and a more stable alternative to hydro is used as the reducing agent. Temperatures of 100C (212F) and a little higher may also be used, where leveling in lighter shades or poor penetration in tighter constructions may be a problem. Towards the end of the dyeing cycle, the temperature might be lowered to 40-50C (100-120F) to increase the percentage exhaustion.
- Time: The time at the maximum dyeing temperature can vary from about 45 minutes at 60C (140F) to about 20 minutes at 100C (212F), but will depend on the amount of circulation in the equipment.
- Salts: Additional sodium chloride or sodium sulfate may be added to dyebaths towards the end of the dyeing in order to improve exhaustion.
- Reducing System: The amounts of caustic soda and hydrosulfite used will depend not only on the concentration of dye present but on the temperature, whether the vessel is open to the air or enclosed, and on the area of exposed surface. The amounts should be sufficient

to maintain the dye in alkaline reduction condition throughout the dyeing. Any additions require care.

- Auxiliary Chemicals: Two kinds of agents which may be used in leuco-vat dyeing are leveling and stripping agents. They are essentially similar in their action, for both interact with the leuco-vat anions in solution to form complexes. These complexes lower the effective concentration of dye anions in the bath and hence can lower the rate of dyeing and increase the rate of stripping. The difference between leveling and stripping agents is one of degree. The stability of the leuco-dye anion/agent complex is greater for stripping than for leveling.

Protective colloids, sequestrants or chelating agents may help facilitate dyeing of greige goods (see the previous subheadings on preparation and water quality).

Prepigmentation

Because the chemicals necessary for vatting make the leuco-vat dye anions in solution highly substantive, there is always the possibility of unlevelness if circulation of the dye liquor is inadequate. But what if dispersions of vat pigments, with no substantivity, were to be circulated and uniformly distributed at the fiber surfaces before alkali and reducing agent were added? Once the pigments were deposited, vatting would result in anion formation just where it is needed, at the fiber surfaces. It would certainly require very fine dispersions, with low particle size distributions, but this problem has already been overcome, and vat pigments are indeed available in such finely subdivided forms. (See the upcoming section in this chapter on commercial forms of vat dyes.)

Prepigmentation (before reduction) is a particularly useful alternative for light and medium shades where levelness might be a problem. Circulation of the pigment can begin at any time and at any temperature between ambient plant temperature and approximately 80C (170-180F); after about 20 minutes the chemicals are added to reduce the dye. Dyeing can then be completed with whatever temperature, time and salt conditions achieve the best results.

Semi-Pigmentation

This is the name given to a process which is a hybrid of the leuco-vat and prepigmentation processes. All the chemicals and dyes required for the leuco-vat process are added and circulated through the goods at plant temperature for 20 minutes before raising the temperature to 60-80C (140-180F) for 30 to 40 minutes. The pigmentary dispersion is slow to reduce at plant temperatures and is simultaneously but gradually deposited while it is reduced as the temperature is raised.

Variations on this theme include the programmed metering of the vatting chemicals into the dyebath, to have total control of the rate of formation of the leuco-vat anion and, consequently, of leveling.

Batch Aftertreatments

Regardless of the vat dyeing process used, once the dyebath has been dropped, the aftertreatments include the following steps: rinsing, oxidation, soaping and neutralization. Softening may be included but is not fundamental.

- Rinsing: This process can be eliminated if the exhaustion is very good, as it might be for pale shades; but with medium shades it is important to rinse out most of the alkali, reducing agents and loose dye; with heavy shades it might be necessary to include one to two grams per liter of both caustic soda and hydrosulfite and a little dispersing agent, in a reductive rinse, for about five minutes at ambient (plant) temperature.
- Oxidation: Usually this is carried out at approximately 60C (170-180F) for about 15 minutes with hydrogen peroxide and acetic acid, or sodium metanitrobenzene sulfonate, or sometimes, perborates.
- Soaping: This is usually carried out at 95C (200F) for about 10 minutes, followed by rinsing. It may be necessary with packages to split soaping into two steps, the first being really a dispersing process conducted at about 60C (170-180F) to ensure that no loose color is available to aggregate and filter out at the second step, which is conducted at normal soaping temperature.
- Neutralization/Rinsing: Depending on whether the oxidation was acidic or neutral, the soaped goods could be neutral or acetic acid rinsed, to ensure that tightly held alkali (particularly in the case of viscose) is not left in the fibers.

Continuous Dyeing Processes

The main economic advantages of continuous dyeing are to be derived from the rapid production of goods with very consistent shade. Speeds of 160 meters (175 yards) per minute are possible. But, the potential benefits have been increasingly curtailed by the shrinking size of individual dye lots, despite successful efforts by machinery manufacturers to make changing colors as painless as possible. When the threaded up length of a nominal continuous dye range may be 400 meters (440 yards), or even more, and the length of a particular dye lot may be only 1800 meters (2000 yards), this spells potential shade consistency problems for the continuous dyer.

A conventional, fully continuous dye range suitable for dyeing polyester/cellulosic, cellulosic and other blended cellulosic fabrics in open width consists of at least 11 separate pieces of dyeing equipment strung together in line. Ideally, goods can be taken up between these pieces, and any piece may be bypassed. The pieces, in order, are: padder, predryer, dryer, thermosol oven, padder, steamer, washer units (must be divisible into four separate sections) and dryer.

Only polyester/cellulosic blends require the thermosol oven treatment in which disperse dyes are fixed onto polyester fibers at 200-215C (390-420F). The thermosol process will be discussed in a later chapter entitled Dyeing of Blended Fibers and Fabrics.

The author regrets that this is not the place to discuss the engineering aspects of so many types of equipment, particularly since such knowledge would be valuable to plant engineers and dyers alike. It is an ongoing concern of AATCC that its constituency has been poorly served by publications in this area, and the association would like to remedy this situation. For an exception, see (*6*).

The principle dye range configurations used for cellulosic fiber dyeing are called the pad-steam (or pad-dry-steam) and wet-on-wet (or pad-pad-steam) processes.

Pad-Steam Process

The pad-steam process for continuously dyeing vat dyes is suitable for most flat cellulosic fabrics. Here a vat pigment dispersion is padded onto the goods and dried. A wet pickup of 60-70% might be suitable for many cotton and polyester/cotton flat goods. This process would be unsatisfactory for corduroy and terry cloth because the pigment will migrate to the fabric surfaces during drying. In addition to the issue of migration is the adverse surface effect (flattening, distortion) if goods are not run wet-on-wet, avoiding predrying and drying cans.

The goods are then padded with alkali and reducing agent, enter the steamer, where vatting and leuco-vat anion diffusion take place, and are then successively rinsed, oxidized, soaped and rinsed through the four sections of washing units, followed by drying.

Wet-on-Wet Process

The wet-on-wet process is only suitable for those fabrics which have the ability to retain large amounts of water. These include terry cloth and some styles of corduroy. The adverse surface effects of flattening and distortion are avoided by not passing these goods through the predryer and over dry cans. So is the cost of driving off very large amounts of water. The process parallels the pad-steam process, but without the drying between padders. It relies on the goods, which enter the second pad with a wet pickup of 60 to 70% of the vat pigment dispersion, leaving the second pad with a higher total wet pickup of 100 to 200%. The increase in wet pickup, the differential wet pickup, ensures that some alkali and hydro are added to the pigment to facilitate subsequent reduction in the steamer. Problems can arise from interchange of the two pad liquors in the second pad trough. This differential pickup criterion cannot be met by much flat goods, which have low water inhibition, but is fine for terry cloth and corduroy.

Padding

The function of padding is to mechanically place the aqueous compositions of dyes and/or chemicals where they are required, uniformly across the goods from side to side, by saturating the fabric in the pad bath and then squeezing off the excess pad liquor. This process should leave a known amount of material held uniformly by the wet fabric along its length and width provided that:

- The wet pickup is constant from side-center-side of the fabric, which is dependent on the adjustment of the squeeze rolls of the padder.
- The immersion time remains constant and the goods are uniformly wettable. For this, good preparation is required.
- The liquor temperature and composition remains constant. The latter depends on whether the dyes or chemicals are attracted preferentially out of the pad liquor, by the fibers. Pigments have no fiber substantivity, so there should be no problem with vat dispersions.

Predrying and Drying

In order to control migration of vat pigment particles to the fabric drying surfaces, a number of precautions are necessary.

- The heat in the dryers should be as uniform as possible from side-center-side and from back-face, for the water carrying the dispersion will preferentially travel towards the area of highest water evaporation rate, and
- The pad liquor should contain an antimigrant. An antimigrant causes flocculation and aggregation of the pigment particles as the pad liquor becomes concentrated by drying. The flocculated pigments are not sufficiently mobile to move rapidly towards the drying surfaces along the fiber and fabric capillaries. The propensity for a particular pad liquor to encourage or discourage migration can be checked using AATCC Test Method 140-1990 (*7*).

Among other things, particulate migration is very dependent on fabric structure, moisture content, air and moisture movement in the dryer and the particle size distribution of the vat pigment.

Steaming

A normal steaming time would be between 30 and 60 seconds. The steamer should contain air-free, saturated steam very slightly superheated; e.g., with a wet bulb temperature that of the boiling point of water, and a dry bulb temperature no more than about 5C (9F) higher.

The steamer should be equipped with a water seal at the exit end through which there should be a constant flow of water sufficient to maintain the temperature at not more than 40C (105F).

Increasing the time of steaming may decrease the appearance of depth of shade without lowering the percentage of dye fixed. This may relate to dye diffusing deeper within the fiber bundles, and losing its effect on the surface color with increased steaming.

Aftertreatment

Washer units come in a variety of configurations, but whatever type they are they must be separable into four distinct groups in which the functions of rinsing, oxidizing, soaping and rinsing/neutralizing may be performed separately before the final drying.

Semi-Continuous Dyeing Processes

If any one step in a batch dyeing process is carried out continuously, then the term semi-continuous can be applied to the overall dyeing process. For example, cotton fabrics to which vat pigments have been applied by padding followed by drying may have the shade developed by transferring the goods to a jig where vatting, leuco-vat diffusion into the fiber, rinsing, oxidation, soaping and rinsing can be effected.

Dyeing polyester/cotton and other blended fabrics has other examples of selectively using sections of the continuous dye range, all of which can contribute to the efficient use of both continuous and other batch dyeing equipment, as well as to processing versatility.

About This Series

THIS is the fifth installment in this series of papers on dyes and their application. Previous installments have covered the application of anions to nonionic fibers (October 1991), direct dyes (November and December) and the first portion of this chapter on vat dyes (January 1992). The series is intended to serve as an introductory text and source book for those who want to expand their understanding of the technology of dyeing and coloration. The author, a frequent contributor to TCC and a member of its Editorial Board, is a professor of textile chemistry at Clemson University.

Continuous Warp Dyeing of Indigo

The principles of dyeing ball warps, warp beams or piece goods with the leuco-indigo anion are easy to understand, and the present processes result from the low substantivity of the anion for cellulose. For examples, see Kramrisch (*8*) and also (*4*).

The dyeing equipment consists essentially of a series of open wash boxes equipped with multiple upper and lower rolls, around which the goods are led in a serpentine path, with squeeze rolls between the boxes. Above the middle set of four to six boxes (vats) skying rolls are provided. The process is carried out at ambient temperature.

After wetting out the goods in a first boxes, they pass at about 25 meters per minute to the middle set of boxes and are immersed in leuco-indigo dye liquors for 10 to 30 seconds, squeezed to about 100% wet pickup, and skyed for about two minutes. These three steps are repeated in successive boxes, as many times as desired, up to about six. In each box some more leuco-indigo is imbibed, followed by air-oxidation, and the indigo pigment is gradually built up, primarily on the fiber surfaces.

The indigo is usually dissolved in a stock vat which contains indigo (100%), caustic soda and hydrosulfite at concentrations of about 80, 70 and 60 grams per liter. The stock vat is used to supply the boxes (vats), which are preset with caustic and hydrosulfite, to maintain a level of: indigo (100%), caustic soda and hydrosulfite, at concentrations of about 5, 2 and 1.5 grams per liter. The heart of the process is in the circulating of the liquor in the vats and metering-in stock dye and chemicals to maintain constant, uniform dyeing conditions. The dyeing is concluded by carrying the goods through several boxes of counterflowing water.

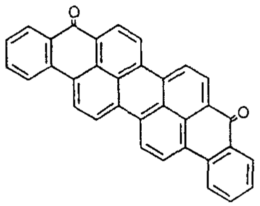
Vat Dyes

Earlier, the redox properties of vat pigments were discussed at some length. Vat pigment molecules generally have from one to three pairs of groups, suitable for reducing to soluble leuco-vat anions (see Table I and Fig. 2 from Part 1 of Chapter 3 and Fig. 1 in Part 2 of the Chapter 3) but the chemical entities carrying these reducible groups are pretty complex.

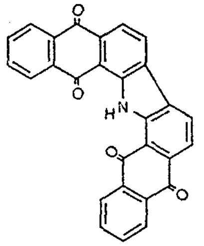
Chemical Structures

The structures of all anthraquinonoid vat dyes are characterized by having at least five and sometimes more than ten aromatic rings, many of them condensed together. Most vat dyes have seven to nine rings. The structures of the anthraquinonoid vat dyes in the U.S. market today fall into four principal chemical subgroups:

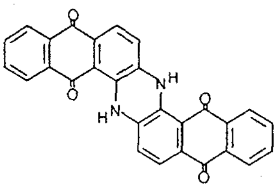
- Violanthrones: The structure of violanthrone, C.I. Vat Blue 20, is shown in Fig. 1a. Dyes based on this structure



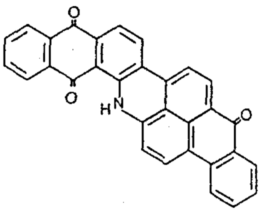
a) Violanthrone



b) Anthraquinone Carbozole

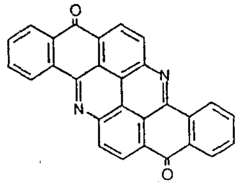


c) Indanthrone

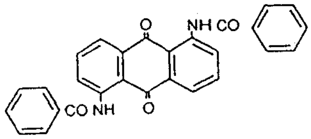


d) Benzanthrone Acridone

Fig. 1. The parent structures of the four principle chemical sub-groups of anthraquinonoid vat dyes.



a) Yellow 1



b) Yellow 3

Fig. 2. Two C.I. vat dye structures.

include C.I. Vat Blues 16, 18, 19 and 20; C.I. Vat Greens 1 and 9; and C.I. Vat Blacks 9 and 16.

- Anthraquinone Carbazoles: A simple carbazole, C.I. Vat Yellow 28, is shown in Fig. 1b. Dyes based on this structure include C.I. Vat Oranges 11 and 15; C.I. Vat Green 8; C.I. Vat Browns 1 and 3; and C.I. Vat Black 27.
- Indanthrones: The parent member of this family, C.I. Vat Blue 4, (b.1901), shown in Fig. 1c, has been mentioned earlier, and is joined by the offspring, C.I. Vat Blues 6, 12 and 14.
- Benzanthrone Acridones: The basic structure is shown in Fig. 1d). Dyes based on this structure include C.I. Vat Green 3 and 13; and C.I. Vat Black 25.

Substituent Groups

Nitrogen often participates in the aromatic ring structures of vat pigments (compare Fig. 1b, c and d, and in Fig. 1a and b from Part 1 of Chapter 3). Oxygen and sulfur do so less often. Apart from the pairs of reducing groups (called quinones), vat pigments are singularly free from substituent groups. Some chloro (–Cl) and bromo (–Br) substituents, some hydroxy, methyl and methoxy groups, (–OH, $-CH_3$, $-OCH_3$), and a few amido groups, –NH.CO–, take care of most contingencies. The absence of ionic solubilizing groups goes (almost) without saying. This should make drawings of vat pigment structures easy to recognize. For example, could either of the structures represented in Fig. 2 be a vat dye?

Commercial Forms of Vat Dyes

Vat dyes as sold are usually water insoluble pigments. These pigments are made in the form of either readily dispersible powders or as ready to use aqueous pastes or liquids (not solutions). To achieve the desired particle size distribution requires extended milling in the presence of a dispersing agent, which frequently is sodium lignin sulfonate, with or without other anionic surfactants. About 50% of the particles in a good vat dye dispersion have diameters of one micron or less; i.e., 1×10^{-6} meters (*4*).

Powders

Vat dye powders fall into two principle groups: those which can be used for either batch or continuous processes in which the fibers are pigmented prior to color development, and those with a high color content, relatively low dispersing agent and low fine particle content. Such powders are unsuitable for processes which involve fabric pigmentation.

Pastes or Liquids

Vat dyes in the form of pastes and liquids are most frequently used in continuous dyeing in the U.S. Powders are preferred in Europe. Vat dyes can be purchased in combination with disperse dyes for dyeing polyester/cotton blends continuously with vat disperse dye combinations, standardized by the manufacturer to give good union shades.

Solubilized Vat Dye Powders

Vat dye makers have always been aware of how desirable it could be to have readily water soluble products, and for many years water soluble derivatives of vat dyes have formed a complete class of dyes unto themselves. They are called solubilized vat dyes. Such dyes are made by reacting vat-acid forms of some vat dyes to make the corresponding water soluble sodium salts of the sulfate esters. The functional group can be drawn as:

$$= \backslash CC{-}O{-}SO_3{}^{-}Na^{+}.$$

From these water soluble anionic compounds, the original pigment can be restored by oxidation with acidified sodium nitrite (*2*). Economic considerations have almost completely eliminated these interesting vat dye derivatives from the U.S. market (*1*).

Review

The diversity of the dyeing methods now possible, starting with the chemically complex but exceedingly stable vat pigments, is a tribute to the ingenuity of dye application chemists. However, vat dyes are expensive. Their color gamut is restricted and the strongly alkaline reducing environment is not compatible with most other dyes and some fibers. So, despite excellent fastness characteristics, their utility is self limiting, like that of all other dye application classes for cellulose. ∞

References

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