Flow Rate, Affinity and Levelness in Exhaust Dyeing: An Analysis Based on System Kinetics

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Perpetual demand for shade uniformity within dyed textile materials places unremitting pressure on the dyer's skill. Experience has often taught the successful dyer which dyes and procedures will result in the production of reproducible and uniform shades. But, as has been previously observed, past success with one group of fibers or dyes need not guarantee future success with other groups of fibers or dyes. Hardly any dyeing technologist would disagree with the view that there is no substitute for old fashioned practical experience, but to be successful in the international market, the dyer must have more than just experience-based knowledge. When the dyer supplements practical experience with an understanding of the physico-chemical characteristics of various dyeing systems, technical problems are avoided and problem solving skills enhanced.

The interrelationships that exist among dyebath flow rate, dye affinity and resulting levelness in exhaustion dyeing processes are explored. It is hoped that this analysis, which is based in part on the mathematics of diffusion, can be useful in illustrating the fundamental relationships involved.

Dyebath Types

There are three fundamental forms of dyebaths—infinite, finite and transitional. The essential characteristic of infinite dyebaths is that the concentration of dye in the bath and at the fiber surface does not change during the course of diffusion of the dye into the fiber during the entire time of dyeing. On the other hand, finite dyebaths are characterized by a continuously decreasing concentration of dye in the bath and at the fiber surface during the course of dyeing until an equilibrium concentration between the dyebath and the fiber surface is achieved. Transitional dyebaths are those that start out as infinite baths but change to finite baths during the course of sorption of dye by the fiber during the dyeing process.

Sorption of indigo by cotton denim yarn in commercial indigo dye ranges occurs from infinite baths, since the indigo that is sorbed by the cotton fiber from the dyebath is continuously replenished. Exhaust dyeing of cellulosic fibers with conventional vat or direct dyes occurs from finite baths. Dyeing of hydrophobic fibers with dispersed or basic dyes can occur under infinite, finite, or transitional dyebath conditions—depending greatly on the concentration of the dye and other well defined parameters.

Four Steps in Dyeing

For each of the three dyebath forms discussed above, there are four fundamental steps involved in the transfer of dye from the dyebath to the fiber. These four steps are illustrated by the simplified schematic shown in Fig. 1. The four steps may be summarized as follows.

Step 1: The dyebath flow carries the dissolved dye to the immediate region of the fiber. As the fiber is approached more and more closely, flow decreases and velocity gradients develop. The velocity of the bath changes from that which exists in the bulk of the solution to that which exists at the fiber surface. The region of change of dyebath velocity from that which exists in the bulk of the dyebath to that which exists at the fiber surface is referred to as a hydrodynamic boundary layer. The “thickness” of such a hydrodynamic boundary layer is highly dependent on the velocity of flow of the bath past the fiber surface.

Step 2: As dissolved dye diffuses through the hydrodynamic boundary layer and is sorbed by the fiber, the concentration of dye changes from that which exists in the bulk of the dyebath to that which exists at the fiber surface. The region within the hydrodynamic boundary layer in which this phenomena occurs is referred to as the diffusional boundary layer. Such diffusional boundary layers offer resistance to sorption (or desorption) of dyes by textile fibers. The extent of the resistance that is observed is proportional to the “thickness” of the diffusional boundary layer, which in turn is proportional to the “thickness” of the hydrodynamic boundary layer.

Step 3: After the dye has diffused through the diffusional boundary
layer, the dye is rapidly sorbed by the fiber surface, and then
*Step 4: Diffuses to the interior of the fiber. A much more detailed discussion of diffusional boundary layer phenomena is available.3

**Diffusional Boundary Layer**

The diffusional boundary layer that is depicted in Fig. 1 is at best ideal. Nonuniformity of dyebath flow through real textile materials more often results in a very wide range of boundary layer "thicknesses." A photomicrograph of a small element of a polyester textile material in a flowing, finite disperse dyebath is shown in Fig. 2. The fibers were photographed by use of a special photographic lens that was immersed in a dilute, illuminated dyebath at 130°C. It is clear from the geometric complexity of the fiber mass that the patterns of flow of the bath around and through the fiber mass must be exceedingly diverse.

Distribution of capillary spaces in textile materials through which flow can occur has been reported to be log normal.4 It is possible that a similar distribution of diffusional boundary layer thicknesses may occur during dyeing. Such a hypothetical distribution is illustrated in Fig. 3. However, no matter what the actual distribution of boundary layer thicknesses may be, it is clear that there is likely to be both a mean value that characterizes the overall dyeing system and other values that characterize deviations from the mean. It is probable that the uniformity of dye uptake or levelness is influenced strongly by the presence of wide differences in flow related boundary layer thicknesses throughout a textile mass.

**Dimensionless Parameters**

Fractional uptake of dye, $M_t/M_\infty$, where $M_t$ is the concentration of dye in a cylindrical fiber at a given time, $t$, and $M_\infty$ is the concentration of dye in the fiber at equilibrium, can be expressed by the following functional relationship:

$$M_t/M_\infty = \text{f}(D_f t/r^2, E_\infty, L) \quad \text{Eq. 1}$$

where $D_f t/r^2$ is a dimensionless time parameter in which $D_f$ (cm²/s) is the constant, concentration-independent diffusion coefficient of dye in the fiber; $t$ (s) is the time of dyeing, and $r$ (cm) is the radius of the fiber. The group, $D_f t/r^2$, is referred to as a dimensionless time parameter since all of the dimensions cancel and the only variable term is $t$. The term, $E_\infty$, is the fractional equilibrium exhaustion of the bath given by:

$$E_\infty = (C_0 - C_\infty) / C_0 \quad \text{Eq. 2}$$

where $C_0$ and $C_\infty$ are respectively the initial and equilibrium concentration of dye in the bath. The dimensionless parameter, $L$, is given by:

$$L = (D_f r)/(D_f t \cdot K \cdot \delta_f) \quad \text{Eq. 3}$$

where $D_f$ (cm²/s) and $D_f$ (cm²/s) are respectively the diffusion coefficients of the dye in the bath and the fiber; the dimensionless parameter, $K$, is the equilibrium distribution coefficient of the dye between the fiber and the bath; the radius of the fiber is given by $r$ (cm), and $\delta_f$ (cm) is the thickness of the diffusional boundary layer. The parameter $L$ is often referred to as dimensionless boundary layer, since all of the dimensions cancel. The only variable term shown on the right hand side of Eq. 3 for a given dyeing system is $\delta_f$, which is highly dependent on dyebath flow. As flow increases.

![Fig. 1](image1.png)

![Fig. 2](image2.png)

![Fig. 3](image3.png)

![Fig. 4](image4.png)
more and more, the thickness of the boundary layer approaches zero, and the value of the parameter \( L \) approaches infinity. In practice the effective boundary layer may have dimensions comparable with those of a yarn rather than a fiber. It must be stressed here that the present analysis is for fully accessible fibers.

Although no formal diffusion equation solution is available that permits the computation of \( M_t/M_\infty \) as a function of \( D_f t/r^2, E, \) and \( L \), a technique has been proposed that permits iterative calculation of \( D_f t/r^2 \) as a function of \( M_t/M_\infty, E, \) and \( L, \). The technique has been used by Hou et al. \(^6\) to construct a series of tables and is summarized in the next section.

**Computational Procedure**

Linear transitional systems are distinguished from other sorption systems by having two forms of fractional diffusant uptake at the point of transition. \(^2\) The two forms are fractional equilibrium uptake for finite bath conditions, \( (M_t/M_\infty) = f_w \), and fractional saturation uptake for infinite bath conditions, \( (M_t/M_\infty) = f_{sat}. \) The two quantities are related to each other for a given value of \( \alpha \) by:

\[
f_{sat} = \alpha f_w/(1 + \alpha - f_w) \quad \text{Eq. 4}
\]

where the alpha term is given by:

\[
\alpha = (1 - E_w/E) \quad \text{Eq. 5}
\]

Under the assumption that all fractional uptake values for a finite bath system can be treated as if they were transitional values, dimensionless values of time, \( (D_f t/r^2)_0 \), can be estimated for each value of \( M_t/M_\infty \) for given values of \( \alpha \) and \( L \) by:

\[
(D_f t/r^2)_0 = (D_f t/r^2)_1 + [(D_f t/r^2)_1 - (D_f t/r^2)_{eq}] \quad \text{Eq. 6}
\]

where \( (D_f t/r^2)_{eq} \) is the value of dimensionless time calculated by the use of Wilson’s equation \(^9\) for a given value of \( f_w \) and \( \alpha \) when dyebath flow is so very high that there is no boundary layer and \( L \) therefore equals infinity; \( (D_f t/r^2)_{eq} \) is the value of dimensionless time calculated by the use of Newman’s equation \(^10\) for corresponding values of \( f_{sat} \) and a given value of \( L \), when \( \alpha \) equals infinity, and \( (D_f t/r^2)_{eq} \) is dimensionless time calculated by the use of Hill’s equation \(^11\) for corresponding values of \( f_{sat} \) when both \( \alpha \) and \( L \) are equal to infinity.

**Dimensionless Halftime**

Eq. 6 has been used to calculate the value of dimensionless time corresponding to \( M_t/M_\infty = 0.5 \) for various values of \( E_w \) and \( 1/L \). Again, it should be noted that when dyebath flow is very high, the thickness of the diffusional boundary layer approaches zero and \( L \) approaches infinity. As \( L \) approaches infinity, \( 1/L \) approaches zero. Dimensionless halftimes as a function of \( 1/L \) and \( E_w \) are plotted on a logarithmic scale in Fig. 4. It is revealed that halftime is much more sensitive to \( 1/L \) or flow for high values of equilibrium dyebath exhaustion than for low values of equilibrium exhaustion.

**Fractional Dye Uptake**

Although Fig. 4 is useful for illustrating that halftime is more sensitive to flow or \( 1/L \) for those dyebaths having very high equilibrium exhaustion, it is useful to show the effect of \( L \) and \( E_w \) on values of \( M_t/M_\infty \) other than 0.5. In Fig. 5 values of \( M_t/M_\infty \) over the range of 0.1 to 0.95 are plotted as a function of the square root of dimensionless time on a log scale for two values of \( L \) and two values of \( E_w \).

The two \( L \) values of infinity and 20 could conceivably be approximated in conventional commercial dyeing systems. The \( L \) value of infinity is approached in a bath flowing with such high velocity that the diffusional boundary layer approaches zero at the fiber surface. However, the \( L \) value of 20 corresponds to that found in a bath having less than optimum dyebath flow and a significant diffusional boundary layer at the fiber surface.

The \( E_w \) value of 0.985 corresponds to that for a dye that has very high affinity for the fiber, leading to a very high level of equilibrium dyebath exhaustion. On the other hand, the \( E_w \) value of 0.84 corresponds to that for a dye that has only moderately high affinity for the fiber, leading to only moderately high equilibrium dyebath exhaustion. It is shown in Fig. 5 that the rate of uptake of dye from the dyebath having very high equilibrium dyebath exhaustion is much more sensitive to differences in flow than is the rate of dye uptake from the dyebath having only moderately high equilibrium dyebath exhaustion. This behavior is consistent with that which is observed in practice, for example, it is more difficult to obtain level dyeings with dyes that have very high affinity.

It should be noted that the four rate of uptake curves given in Fig. 5 are for independent fibers in separate dyeing systems. Computation of rates of dye uptake in different sections of a textile material in a common dyebath as a function \( L \) and \( E_w \) is more difficult. For such real systems it is to be expected that the effect of flow rate differences per se on levelness will be magnified. Localized exhaustion of dye in one part of the textile will lead to depletion of the dyebath. Under such conditions, the dye-starved dyebath will provide little dye for other sections of the textile and levelness will be impaired further.

Although the present discussion has been limited to sorption of dye by fibers, it should be noted that the analysis also can be applied to dye desorption processes. Desorption of dye also is strongly influenced by boundary layer phenomena, and this fact can influence migration of dye from fibers of a given dye content to other fibers that may have lower dye contents.

**Practical Consequences**

In commercial package dyeing of cellulose, polyester, and acrylic fiber with vat, disperse, and basic dyes, experience has shown the writer and others that the use of dyebath addi-
atives that will significantly reduce the equilibrium exhaustion of the dyebath can dramatically improve the levelness of the final dyeing. In the case of vat dyeing of cotton, the addition of polyvinylpyrrolidone to the dyebath permits the level dyeing of pastel shades with extremely high affinity vat dyes. In high temperature dyeing of polyester fiber with disperse dyes, the use of polyethoxylated castor oil can have a pronounced beneficial effect on the levelness of the final dyeing. Cationic compounds such as guanidine hydrochloride are widely used in dyeing acrylic fibers with basic dyes to promote levelness by impeding exhaustion.

Concluding Remarks
It is hoped that the discussion of the interrelationship between dyebath flow rate, dye affinity, and resulting levelness that has been presented will serve to stimulate experimental research in the area. The present discussion has been based primarily on a mathematical analysis in which the classical diffusion equation solutions have been employed. Nevertheless, the results of the analysis seem to at least partially explain that which is widely observed in practice—high affinity dyes are difficult to apply uniformly unless suitable dyebath auxiliaries are used.

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References

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