Reactive Dye Selection and Process Development for Exhaust Dyeing of Cellulose

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ABSTRACT

In dyehouses processing cellulosic fibers with reactive dyes, much progress has been made in the quest for zero defect production by the introduction of controlled coloration techniques which support level dyeing performance.[1] There is however, still room for further improvement, especially in the area of shade reproducibility. Shade reproducibility can be significantly improved by considering the compatibility of the dyeing profiles of the dyes selected. By studying the properties of dyes during the primary and secondary exhaustion phases of the process and their reactivity, the measures and levels of performance required to achieve right-first-time production can be defined.

The Reactive Dye Compatibility Matrix (RCM) can be used to define the optimum dyeing profile for exhaust dyeing with reactive dyes, quantify dye migration properties, the degree of process control required to achieve shade reproducibility and level dyeing performance, and an index of dye reactivity. Understanding the RCM will allow dyes with similar properties to be identified and used in combination to support right-first-time production. It can predict the performance of dyes on the most recently introduced dyeing machinery and in new application techniques which have been designed to minimize the impact of reactive dye systems on the environment. It can also be used as a diagnostic tool when optimizing application techniques.

KEY TERMS

Exhaust Dyeing
Process Development
Reactive Dye Compatibility Matrix

Retailers and clothing manufacturers are commanded to improve financial performance by minimizing working capital and price mark downs for surplus garments by accurate forecasting of sales using techniques such as electronic point of sale. Shareholders of textile companies demand improved profit performance and international competitiveness. The "green lobby" demands a reduction of the environmental impact produced by the textile industry. These pressures have focused attention on the need for right-first-time production and elimination of waste at all stages of the textile production chain. The impact of these changes has resulted in multiphase fashion sales seasons, smaller production lots, and reduced delivery times to support stock replenishment. These trends make the level of right-first-time production the key measure of performance for the industry.[2,3]

The trends to lower liquor ratios to increase productivity through reduced filling, draining, heating and cooling times, and to reduce chemical, energy and effluent costs, has placed greater focus on dye performance and application techniques.

The search for product differentiation in leisure and activewear has resulted in increased use of mercerized cotton and cellulosic blends with elastomeric and microdenier fibers, which have a reputation of being difficult to process and require pristine fabric appearance, dimensional stability and high levels of wetfastness.

The Reactive Dye Compatibility Matrix (RCM) can be used to define the optimum dyeing profile for exhaust dyeing with reactive dyes, quantify dye migration properties, the degree of process control required to achieve shade reproducibility and level dyeing performance, and an index of dye reactivity. Understanding the RCM will allow dyes with similar properties to be identified and used in combination to support right-first-time production. It can predict the performance of dyes on the most recently introduced dyeing machinery and in new application techniques which have been designed to minimize the impact of reactive dye systems on the environment. It can be used as a design tool when developing new application techniques or when optimizing bulk processing conditions.

Dye Selection Criteria

Accurate and consistent standardization of dyes is the principle requirement for optimized dyehouse efficiency and right-first-time production.

Working toward a total pass/fail tolerance of ΔE 1.2 (CMC), a significant proportion, ΔE 0.9, has been estimated to be taken up by the expected small variations in processing parameters and raw material. This leaves only ΔE 0.3 for accuracy of dye standardization. A statistical analysis which assesses the effect of dye standardization limits on right-first-time production is shown in Fig. 1.[4]

Exhaust dyeing of cellulose with reactive dyes is a complex process. It involves the exhaustion of the dye onto the fiber in the presence of electrolyte and then the addition of alkali to promote the chemical reaction between the dye and cellulose. The external factors which influence the process have been identified and segregated into assignable and random variables.[1]

The assignable variables include the internal fabric pH at the start of the dyeing cycle, the liquor ratio, the temperature gradient, the fixation temperature, the electrolyte concentration, the

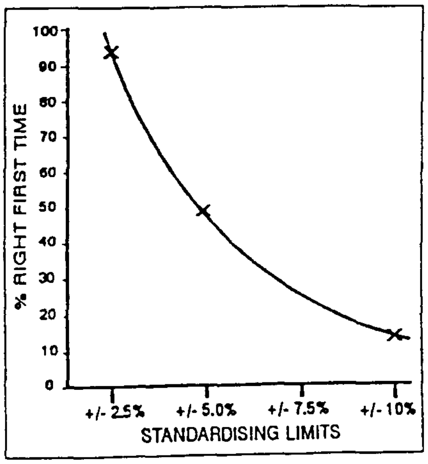

Fig. 1: Effect of dye standardization on the probability of right-first-time production.

addition profiles of dye, electrolyte and fixation alkali, the fixation pH and time. They can all be controlled and measured either by simple manual tests or by microprocessors. The random variables are the impurities in cotton, water supply, chemicals, and the dyes selected to reproduce the target shade. The control of these random variables often requires intervention of trained personnel.

The controlled coloration approach has proven to be the basis of a systematic, structured and successful approach to improve the right-first-time production rate. The level dyeing performance of reactive dyes has benefited from the introduction of controlled coloration and it is now perceived that shade reproducibility is the major obstacle preventing zero defect production.

The performance of a reactive dye is defined by the S.E.F. profile as shown in Fig. 2. The substantivity equilibrium, *S*, represents the primary exhaustion of the dye in the presence of neutral electrolyte. The exhaustion equilibrium, *E*, represents the final exhaustion of the dye which takes place after the addition of the fixation alkali. The fixation value, *F*, represents the fixation level for the dye. The secondary exhaustion, represented by *E-S*, takes place simultaneously with dye fixation after the addition of the fixation alkali.

Dyes with a wide range of S.E.F. profiles can be obtained. Dyes with *S* values as high as 96% and as low as 17% are commercially available. Dyes with such wide differences in substantivity will exhibit different levels of performance and sensitivity to external influences. Dyes with low substantivity will generally be more sensitive to variations in liquor ratio and electrolyte concentration. In contrast, dyes with high substantivity will be robust and provide shade stability to these variations in processing conditions.

During the initial phase of the process, the neutral primary exhaustion of the dye in the presence of electrolyte, migration and diffusion can take place. Dye which has exhausted onto the fiber is available for migration, and leveling will take place by the classical mechanism. The actual migration which takes place during primary exhaustion will depend on the chemistry of dye—its molecular structure, physical chemistry and stereochemistry, and on external factors—concentration of the dye added to the dyebath, time, temperature, liquor ratio, rate of liquor circulation and fabric construction, or in the case of yarn dyeing, package format. From practical considerations it is the chemistry of the dye which has the dominant influence on migration properties and therefore on its level dyeing performance.

The migration properties of dyes are easily measured using a simple laboratory test. A schematic description of the test is given in Fig. 3. Using color measurement techniques to measure the depth of shade of the test samples D2 and B2 it is possible to calculate a migration index, *MI*, as in Eq. 1.

$$\text{Migration Index (MI)} = \frac{\text{strength B2 x 100}}{\text{strength D2}} \qquad \text{Eq. 1}$$

The migration index defines the migration properties of an individual dye applied by a defined process. A dye with ideal migration properties in a defined process will possess a *MI* of 100.

The substantivity equilibrium values, *S*, and migration indices, *MI*, for a series of blue dyes and red dyes applied by the manufacturer's standard recommendations are given in Table I.

The chromophore of the blue dyes is similar. The differences in substantivity equilibrium values and the migration properties are due to differences in the molecular weight of the dyes, their stereochemistry and their reactive system. The series of red dyes also have similar chromophores and the differences observed in their performance are due to the chemistry of the individual dyes.

This data shows that there is an optimum substantivity equilibrium value of between 70-80%. In this range, the affinity of the dyes for cellulose is such that optimum dye migration properties are obtained. For dyes with these properties an even distribution of color will be achieved at the stage in the process just prior to the addition of the fixation alkali.

For dyes with a substantivity equilibrium value of greater than 80%, the higher affinity of the dye for the cellulose results in inferior migration and level dyeing properties during the primary exhaustion phase. Dyes with lower substantivity equilibria may have good migration properties but will have a significantly lower influence on level dyeing performance because of the reduced concentration of dye on the fiber.

Probably the most critical stage of the reactive dyeing process is the addition of the fixation alkali. It is especially critical for dyes with a high (*E-S*) value. For these dyes, the addition of alkali increases the substantivity of the dye and exhaustion and rapid fixation take place simultaneously. The

Table I. Substantivity Equilibrium Values and Migration Indices

Dyebaths Based on C.I. Reactive	%S	%MI
Blue 171	87	60
Procion Navy H-EXL	73	90
Blue 184	66	81
Blue 222	53	74
Blue 225	42	91
Blue 238	39	89
Red 141	87	51
Red 55	82	87
Procion Crimson H-EXL	74	100
Red 184	56	80
Red 195	30	90

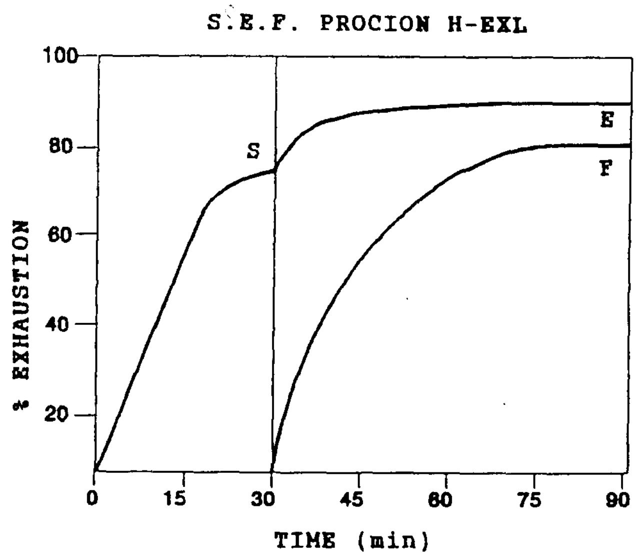

Fig. 2. S.E.F. profile.

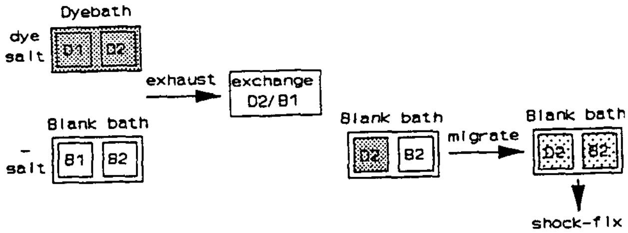

Fig. 3. Migration test.

rate of fixation must be controlled by the use of complex and time-consuming addition profiles. This requires the use of metering systems to achieve linear fixation of the dye which is necessary to secure level dyeing performance.[5] The migration which can take place during the secondary exhaustion phase of the process is severely restricted due to the rapid fixation of the dye and will not significantly contribute to level dyeing performance. Thus for a dye with a high secondary exhaustion the only control option available to obtain level dyeing is the precise control of the rate of fixation of the dye.[6]

The level dyeing performance of reactive dyes and the degree of control required to achieve level dyeing are governed by the substantivity equilibrium value, the migration which takes place during the primary exhaustion and the secondary exhaustion which takes place after the addition of the fixation alkali. It is possible to quantify the relationship between these parameters, assign a measure of dye performance, and define the degree of control required to achieve reproducible level dyeings, and robust to small expected variations in processing conditions by calculating an empirical value, the Level Dyeing Factor, *LDF*, which is defined in Eq. 2.

$$\text{Level Dyeing Factor, LDF} = \frac{S}{E} \times \text{MI\%} \qquad \text{Eq. 2}$$

While *LDF* values are derived from an empirical equation, the values are consistent with experience and expectations of the performance of dyes which are commercially available. As with the migration indices, *LDF* values reflect the performance of individual dyes applied by a defined process. Table II shows the *S*, *E*, *MI* and *LDF* values for the series of blue dyes previously discussed.

Generally, the *LDF* value will define the most suitable application technique for the dye which will minimize the risk of unlevel dyeing and optimize shade reproducibility. Dyes with high substantivity, low secondary exhaustion, low *MI* values and therefore modest *LDF* values will require controlled addition of the electrolyte after the addition of the dyes. In contrast, dyes with low substantivity, high secondary exhaustion, medium to high *MI* values will possess low *LDF* values. These dyes will require precise control of the liquor ratio, the concentration of electrolyte, and the addition profile of the fixation alkali.

For both groupings of dyes a high degree of process control is required to achieve level dyeing and shade reproducibility. Inevitably, the processes will be long, complex, difficult to manage, restrict production capacity and therefore reduce the profit potential of the dyehouse.

The optimum performance is achieved with dyes of medium/high substantivity, low secondary exhaustion, high *MI* values and therefore very high *LDF* values. These dyes will require the minimum of process intervention to produce level dyeings, provide good shade reproducibility and high rates of right-first-time production. They can be used in a simple process, require only short, simple, linear addition of fixation alkali and will be relatively insensitive to external factors, such as small changes in liquor ratio, electrolyte and fixation alkali concentration.

S, *MI* and *LDF* values provide data on the sensitivity of the dye to external factors such as variations in liquor ratio and chemical concentrations, but to assess the sensitivity of the dye to variations in fixation time and temperature it is necessary to study the reactivity of the dye. A convenient method of assessing the reactivity of the dye is to measure the time taken for half of the dye to react, *T50*. Table III shows the variation in *T50* values for a range of blue dyes applied by the manufacturers' standard recommendations. For this series of dyes the *T50* values vary from 3-14 minutes. For dyes with *T50* values of three minutes the initial rate of fixation is rapid and the addition profile used becomes the critical step to effect level dyeing performance.

In piece dyeing the target rope circulation time for cotton knits is normally two to three minutes. Under these circumstances and in extreme cases, 50% of dye fixation takes place before two rope revolutions and the addition of fixation alkali is completed. In package dyeing, the in-out/out-in directional flow cycle is generally set at 10 minutes; e.g., 3-4 minutes in-out and 6-7 minutes out-in. Again, in extreme cases, 50% of dye fixation takes place before the in-out cycle and the addition of fixation alkali is completed. Such rapid fixation can only put level dyeing performance at risk and therefore precise control is required at this stage of the process. *T50* values will depend on the reactivity of the dye, fixation temperature, and the fixation alkali addition profile. To support level dyeing performance the target *T50* value should be set at a minimum of ten minutes, or, in piece dyeing five rope revolutions, or in package dyeing one complete in-out/out-in cycle.

The criteria for the selection of reactive dyes, which will, when applied using the principles of controlled coloration, maximize right-first-time production are based on *S*, *MI*, *LDF*, and *T50* values.[1] These parameters are the key measures of performance for a reactive dye and represent the RCM. Right-first-time production will be maximized within the RCM set at:

Substantivity in neutral electrolyte	70-80%
Migration Index	>90%
LDF	>70%
T50	10 minutes minimum

Comparisons of these parameters will provide a measure of the compatibility of dyes when they are used in combination. Dyes with similar *S* values, similar and high *MI* values (>90%), similar and high *LDF* values (>70%), and similar *T50* times, will, when used in admixture, exhaust, migrate and react as a single dye. These combinations will be level dyeing, offer high shade reproducibility, be robust to the small expected variations in liquor ratio, electrolyte concentration, fixation pH, time and temperature, and will support the key measure of performance of the dyehouse—right-first-time production.

The RCM has been successfully used to set research targets for Procion H-EXL dyes. With the use of sophisticated molecular engineering techniques it has been possible to design reactive dyes which have the optimum dyeing profile required to maximize the rate of right-first-time production

Table II. Level Dyeing Factor

Dyebaths Based on C.I. Reactive	%S	%E	%MI	%LDF
Blue 171	87	95	60	55
Procion Navy H-EXL	73	90	90	73
Blue 184	66	90	81	67
Blue 222	45	88	74	37
Blue 225	42	96	91	40
Blue 238	39	97	89	36

Table III. Time of Half Fixation, T50 Minutes

Dyebaths Based on C.I. Reactive	Alkali	Addition Profile	T50 (min)
Blue 171	Na_2CO_3	Linear over 10 min.	6.0
Procion Navy H-EXL	Na_2CO_3	Linear over 10 min.	11.0
Blue 184	NaOH	70% progression over 30 min.	10.0
Blue 221	Na_2CO_3	3 equal adds over 20 min.	3.0
Blue 225	Na_2CO_3	70% progression over 30 min.	3.5
Blue 238	Na_2CO_3	70% progression over 45 min.	14.0

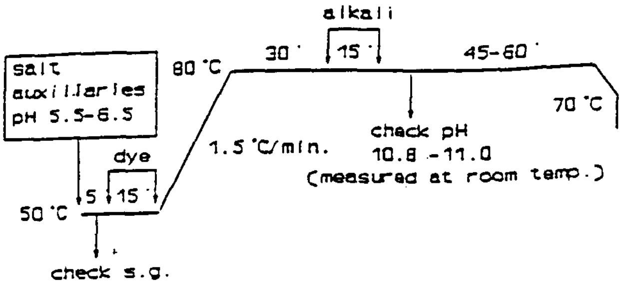

Fig. 4. Standard application profile.

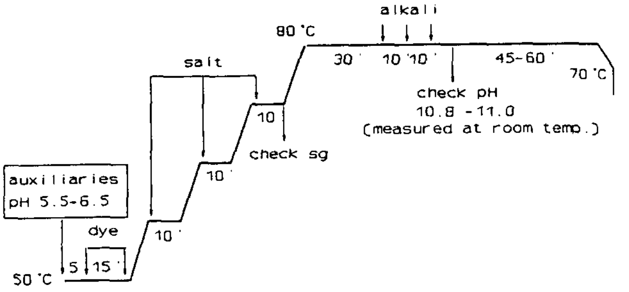

Fig. 5. Portionwise salt application profile.

when exhaust dyeing cellulose. Table IV shows the RCM for these dyes applied by the standard process shown in Fig. 4.

Thus for these dyes it is possible to select combinations of dyes which will support right-first-time production and meet the fastness performance demanded by the highest quality retailers.

Process Design Using the RCM

For a dyehouse which has introduced the concept of controlled coloration and is achieving high levels of right-first-time production the management focus changes towards improving productivity. Control of all variable costs and reduction in the fixed cost/unit of production now become the key measures of performance. To improve performance requires the development of short processes which are simple to operate, easy to control and require the minimum of manual intervention. The RCM has proved to be a valuable diagnostic tool to aid the design of those processes which do not compromise the rate of right-first-time production and offer the required savings in processing time.

Portionwise Salt Process

The established application profile for reactive dyes is based on the portionwise addition of electrolyte and fixation alkali (Fig. 5). It was developed for application at long liquor ratios and for dyeing equipment such as winches and side paddle machines which have low liquor to fiber interchange. The low liquor to fiber interchange on these types of machines demands controlled rates of dye exhaustion and fixation to achieve level dyeing performance. In an attempt to control the rate of dye exhaustion, the electrolyte is added in discrete portions, allowing time for the dyebath to reach equilibrium between the additions. The addition profiles used to retard the exhaustion of the dye range from two or three equal portions made at the starting temperature to complex pyramid addition profiles often made at different temperatures on the temperature gradient. On reaching the fixation temperature a period for dye migration is followed by the addition of fixation alkali. This is generally made in two or three portions, again allowing time for the dyebath to reach equilibrium between additions. The dyeing process is completed by the dye fixation stage. The process is long, complex, labor-intensive, extremely difficult to control and reproduce, and therefore requires a highly skilled and reliable workforce. The complexity of the process is the source of many of the level dyeing and shade reproducibility problems associated with reactive dyes. Furthermore, the process does not exploit the properties of more recently developed reactive dyes especially when applied on more modern jet or overflow machines. Table V shows the RCM for dyes applied by the portionwise salt process.

Portionwise Salt vs. Standard Process

Comparison of Tables IV and V shows that the *MI* and *LDF* values of dyes when applied in a portionwise salt process are not optimized and therefore the process requires precise control to support level dyeing performance and shade reproducibility. The standard is a short, simple process based on a salt-at-start profile and linear addition of fixation alkali.

This process is suitable for medium to heavy shades dyed on unmercerized cotton and does not require exponential microprocessor control of the addition of dyes or chemicals. However, if total automation of machine is available then the isothermal method (Fig. 6) can be used for these shades and substrates.

Isothermal Process

The isothermal process offers further improvements in productivity but because the *MI* and *LDF* values in this process are lower than in the standard process more precise control of the dye addition is required.

Cost and Profitability

The correct choice of processing route has a significant impact on the rates of right-first-time production, variable costs, fixed cost recovery and hence dyehouse profitability. The total cost of production including preparation, dyeing and washing off, productivity analysis and dyehouse profitability for all three methods are shown in Table VI.

In these calculations of the total cost of production the preparation and wash-off processes are identical. It has been assumed that the right-first-time production rate is 100%, and that for the standard and isothermal processes the additional plant capacity generated has been filled.

Table IV. The Procion H-EXL RCM Standard Process

Procion Dye	%S	%E	%MI	%LDF	T50 (min.)
Yellow H-EXL	76	93	90	74	10.0
Red Brown H-EXL	78	92	100	85	10.0
Brilliant Red H-EGXL	76	90	94	79	14.0
Crimson H-EXL	74	92	100	80	10.0
Blue H-ERD	73	93	90	71	10.0
Blue H-EXL	80	94	100	85	14.0
Navy H-EXL	73	90	90	73	12.0

Table V. Procion H-EXL RCM Portionwise Salt Process

Procion Dye	%S	%E	%MI	%LDF	T50 (min.)
Yellow H-EXL	76	93	77	63	10.0
Red Brown H-EXL	78	92	88	75	10.0
Brilliant Red H-EGXL	76	90	81	68	14.0
Crimson H-EXL	74	92	69	55	10.0
Blue H-ERD	73	93	67	53	10.0
Blue H-EXL	80	94	63	54	14.0
Navy H-EXL	73	90	63	51	12.0

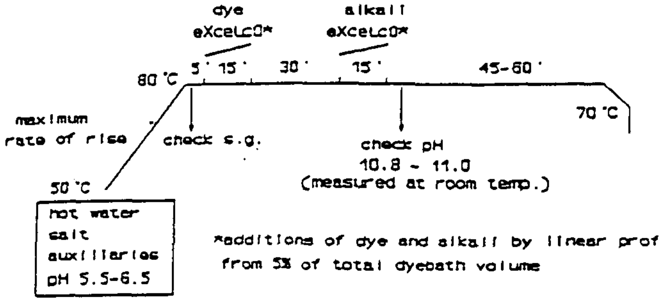

Fig. 6. Isothermal application profile.

Table VI. Cost/Productivity/Profit Analysis

Process	Cost	Productivity	Profit
Portionwise Salt	100	100	100
Standard	95	112	110
Isothermal	94	120	115

Table VII. RCM Procion Navy H-EXL, Standard Process, ULLR

Process	%S	%E	%MI	%LDF	T50 (min)
10:1 Liquor Ratio 70 g/L NaCl	73	90	90	74	10.0
5:1 Liquor Ratio 70 g/L NaCl	79	93	80	68	10.0
5:1 Liquor Ratio 50 g/L NaCl	73	90	91	74	10.0

Table VIII. The Cost of Nonconformance

Process	Cost	Productivity	Profit
Blind Dyeing	100	100	100
Small Addition	110	80	48
Large Addition	135	64	-45
Strip and Redye	206	48	-375

Machinery Developments

The most recent machinery developments from the world's leading innovative machine builders have focused on improving productivity, quality and reducing the cost of utilities (steam, electricity and water), labor and chemical costs. These machines, operating at a 5:1 liquor ratio, can reduce the total cost of processing by 25% compared to a machine operating at a 10:1 liquor ratio.[7] The reduction in the demand for utilities and the reduced chemical usage will minimize the impact of the reactive dye system on the environment. Under these conditions of ultra low liquor ratio (ULLR) the properties of reactive dyes change. At equal electrolyte concentration the substantivity equilibrium is increased due to increased mechanical pickup, and the exhaustion equilibrium and fixation are also increased, but to a lesser extent.[8] However, under these conditions the *MI* and *LDF* values decrease.

The RCM for a navy dye, applied by the standard process at a 10:1 liquor ratio, 5:1 liquor ratio with equal electrolyte concentration and at 5:1 liquor ratio with a reduced electrolyte concentration is given in Table VII. At a 5:1 liquor ratio and 70 g/L salt the *MI* value for this dye falls below the critical value of 90%. To ensure that all the measures of performance within the RCM meet the defined specification to support level dyeing performance, and shade reproducibility, and hence right-first-time production, reducing the electrolyte concentration is the preferred process design option.

Conclusion

Traditionally, many dyehouses are operated assuming that they are labor intensive and with an expectation of poor production efficiency. Processes are often costed with a factor, the cost of nonconformance, to allow for additional processing. The producer who has successfully introduced right-first-time techniques will, without doubt, have the competitive edge in today's dynamic and highly competitive marketplace.

Setting the measures and levels of performance for reactive dyes and defining the Reactive Dye Compatibility Matrix (RCM) will lead to the selection of dyes which will, when applied using the principles of controlled coloration, support the shade reproducibility and level dyeing performance so vital for right-first-time production. The potential reduction in the unit cost of production, improvement in productivity and profit is summarized in Table VIII.

Using the RCM as a diagnostic tool promotes the design of processes which will further improve productivity without putting the levels of right-first-time production at risk. Defining and understanding the RCM is a relatively simple task which is based on simple laboratory evaluations. It will reduce the need for high risk bulk trials to establish processing route options for new fabric/dye/machine combinations. It will also assist in minimizing risk by optimizing established processing routes.

The potential for improved financial performance is high and can be realized by the introduction of quality management systems. Critical success factors will be the commitment and dedication of all dyehouse personnel and the strength of the partnerships which can be forged between customer and supplier.

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