New Trichromatic System For Enhanced Dyeing By The Exhaust Process

By P. Fowler,
DyStar L.P., Charlotte, NC

Introduction

'Right first time' dyeing with reactive dyes requires products having very similar application properties that are little affected by small changes in dyeing conditions. The Remazol RR combination **is** a trichromatic system engineered to meet all these requirements with high cost effectiveness.

Market situation

In the US cotton represents approximately one third of the fiber used in textile processing. Reactive dyes are the most important class of dyes for dyeing and printing cotton and other cellulosic blends They represent about 45% (by value) of colorants used for coloring cellulosic fibers. Reasons for the success of reactive dyes include: flexible application methods, wide range of shades available (including brilliant shades), their fastness properties, and cost-efficiency.

The demands made on reactive dyes are wide-ranging. Requirements depend to a large extent on the specifications' for particular textile articles and on operating conditions (equipment available, legal constraints, etc.). Economic considerations, quality requirements and ecological issues are major factors in the debate concerning the ideal dyeing process and optimum dyestuff selection.

Over 60% of reactive dyes are applied by the exhaust dyeing method. The remainder is applied by padding. The selection of a trichromatic system is of fundamental importance to dyers when choosing reactive dyes for the exhaust process. A wide range of shades can be dyed by combining a single yellow, red, and blue dye. Such combinations can cover over 50% of the shades used for leisure wear.

An important requirement for a trichromatic combination is good reproducibility. Reliable reproducibility is required when recipes are transferred from laboratory to plant conditions, as well as from one batch to another. This is the case even if dyeings have to be performed on different machines and dyeing conditions cannot always be held constant. Moreover, a trichromatic combination should be able to satisfy a wide range of quality requirements. This results in a minimal number of different dyes needed in a dyehouse. To sum up, the main demands made on trichromatic dye combinations are:

- reliable dyeing results
- good reproducibility of shade even if dyeing conditions vary
- good levelness
- *good fastness properties
- flexible application possibilities
- high cost effectiveness

A reactive dye combination that meets these demands is DyStar's new

Figure 1: Chemistry of vinyl sulfone dyes.

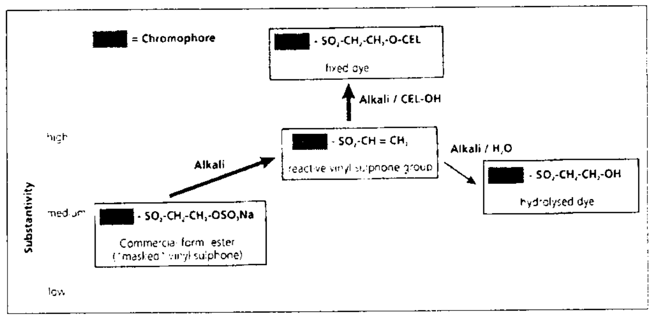
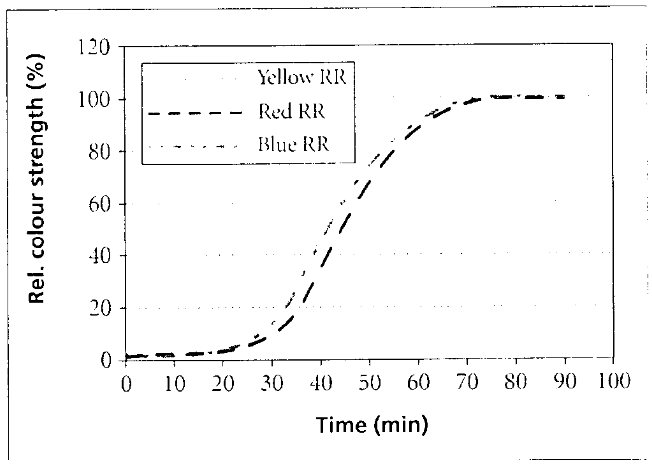


Figure 2: Homogenous fixation behavior of Remazol RR dyes (bleached cotton tricot, automat 60°C, 10:1, alkali dosing 60 min / 50% progression, 50 g/l salt).



Remazol RR trichromatic system. The system is tailor made for exhaust dyeing and has been used successfully throughout the world since its introduction late in 1995.

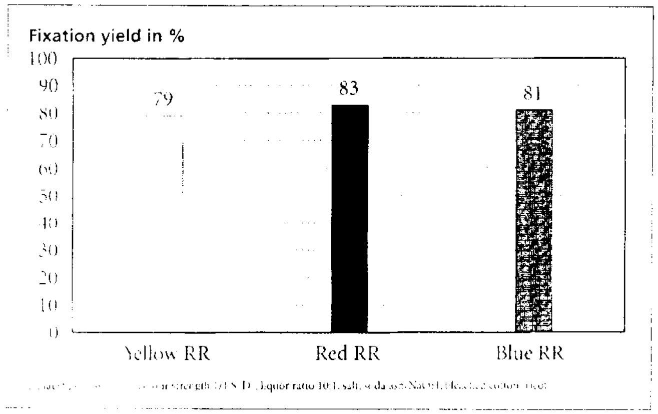
Trichromatic system

State-of-the art production technologies operating within the framework of IS0 9001 are used to manufacture the new dyes. The quality of the intermediates and the production process are monitored and the finished products are standardized using standard test methods to ensure constant quality within the specified tolerances. Factors such as consistency of dye strength and shade are important for good reproducibility.

The new trichromatic system comprises Yellow RR gran, Red RR gran, and Blue RR. gran. These dyes are supplied as low dusting granules, which can greatly improve working conditions in the dyehouse weighing and mixing area. The granules are free flowing and are suitable for use with automatic dosing units.

These dyes also have very good build-up on cotton and man-made cellulosic fibers. Only low concentrations of dye are needed to dye deep shades.

Figure 3: Fixation yields of Remazol RR dyes in the exhaust process.



The good build up of these products makes them very economical, a property that is particularly evident when dyeing deep shades.

These dyes can be used for a wide range of shades. Including a large number of trichromatic fashion shades. In addition to being suited for medium and deep shades, in many instances the new dyes meet the requirements necessary for dyeing pale shades. Thus, we have come a step closer to achieving the goal of producing a trichromatic system for the widest possible shade range.

Our trichromatic system is the result of extensive research and development. In this effort a large number of dyes have been synthesized and tested for use in combination dyeing and as individual shades.

The aim was to develop a trichromatic system for exhaust dyeing at 140°F (60°C). It is interesting to note

Figure 4: Automet dyeing process (60°C)

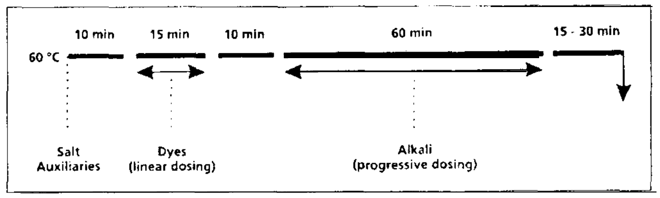
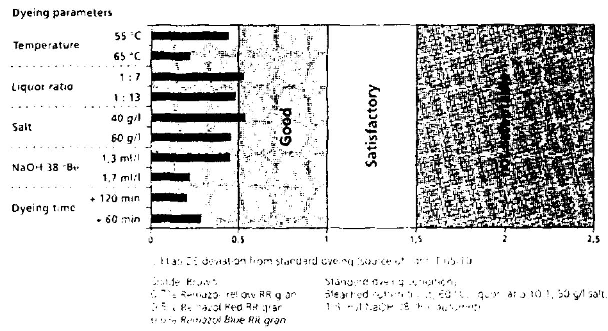


Figure 5: Reproducibility of a dyeing with Remazol RR dyes in fluctuating dyeing conditions (without recipe correction) Figure 6-Washing-off profile of a trichromatic dyeing with Remazol RR dyes.



that research into reactive dyes for exhaust dyeing is increasingly concentrating on the 120-140°F (50-60°C) temperature range because processing costs and dyeing times are lower than for hot dyeing procedures (175" F(8O*C) and above). Almost all fabric qualities can be dyed at 140°F (6O*C), including yarn and fabrics made of mercerized cotton and regenerated cellulosic fibers. However, not all goods can be dyed at temperatures below 120°F (50°C) because low dyeing temperatures can impair the running properties of the goods in jets and affect liquor circulation in package dyeing units.

To achieve optimum reliability and reproducibility of dyeings, two main criteria need to be met:

1. The best possible balance needs to be found between the properties of the members of the trichromatic combination, (i.e. attaining diffusion properties, fixation behavior, and washing-off properties).
2. Normal variations in dyeing conditions should not affect reproducibility.

All three dyes contain at least one vinyl sulfone group as the reactive group. The vinyl sulfone anchor has a significant effect on the dyeing behavior of the dyer. In the commercial product the reactive group IS present in the nonreactive ester form to protect it from being destroyed by premature chemical reactions (Figure 1).

The hydrophilic sulfo groups in the masked reactive group and the hydrophilic groups in the chromophore give these dyes their excellent solubility. They can therefore also be applied at ultra short liquor ratios. The dyes are produced without additives of solubility enhancing organic finishing compounds which would increase the COD load of waste water.

Under standard dyeing conditions in a neutral dye liquor (2% dye, 50 g/l salt, liquor ratio 1O:l. 140*F (60 "C), nonmercerized cotton). these dyes have medium affinity. They have very good diffusion properties on the fiber. This ensures good penetration of the goods and thus level dyeings. Neutral exhaustion and diffusion equilibria are achieved rapidly so the neutral dyeing phase can be relatively short.

In contrast, "hot-dyeing" reactive dyes have high affinity in neutral dye liquors. These dyes have to be applied at elevated temperatures and require longer dyeing times to ensure adequate leveling and diffusion into the fiber. This increases process costs (time) and lowers productivity.

The new dyes in the free vinyl sulfone form have higher affinity than in the ester form and exhaust more completely. The free vinyl sulfone reactive form is generated by addition of alkali. Since these dyes are only moderately reactive, once the dyes have exhausted onto the fibers there is sufficient time for diffusion into the fiber, even under alkaline conditions, before fixation occurs. Progressive dosing of alkali can be used to control the secondary exhaustion phase and fixation rate (Figure 2).

Fixation yield of reactive dyes depends on the dyeing conditions. The following rules of thumb apply:

- higher yields are obtained at lower dye concentrations
- higher electrolyte concentrations result in higher yields
- shorter liquor ratios result in higher yields
- higher affinity between dyes and goods results in higher yields.

High fixation yields are obtained with our trichromatic system even in suboptimal conditions (Figure 3). The relatively low concentrations of dyestuff required to dye specific shades and the comparatively high fixation yield are positive ecological attributes and help minimize the cost of waste water treatment.

Dyeing procedures

The preferred process uses progressively metered addition of the alkali that allows optimum regulation of the dye exhaustion. This does not only apply to vinyl sulfone dyes. The advantages of the automet system are as follows:

- optimum fixation profile
- excellent reproducibility
- excellent levelness
- *short dyeing times
- automated dyeing process
- fewer rejects
- fewer operators required.

Figure 5 shows the 140°F (60*C) automet dyeing process for the Remazol RR system. Following pretreatment of the goods, the salt and auxiliaries are pre-run in the bath and the dyes are then added into the liquor After a short diffusion phase, the alkali dosing program can be started. This should be followed by a final fixation period. As well as cutting out manual errors and dead time, automation greatly reduces the number of rejects.

By varying dyeing parameters such as the salt load, type and amount of alkali, addition profile and duration of individual steps in the process, the dyeing method can be adjusted to suit virtually all article qualities and depths of shades, including articles made of all types of rayon including modal, polynosics, and lyocell (Tencell). Switching the neutral phase to higher temperatures 175/200* F (80/9O*C) is only recommended for articles where penetration is difficult, e.g. high-twist yarns.

The trichromatic system can also be dyed using conventional dyeing procedures. Particular advantages are gained when using the automet dyeing process.

In practice, dyeing conditions are rarely constant. When switching from laboratory equipment to plant equipment and if the same shade is dyed repeatedly either on the same unit or on different units, there are likely to be variations in the following parameters:

*salt load
- temperature
- dyeing time

*type and amount of alkali
- liquor ratio

The new trichromatic system has two major advantages:

1. Normal variations in dyeing conditions do not materially affect the results obtained (Figure 5)
2. Extreme differences in dyeing conditions tend to affect the strength of the dyeing rather than the shade obtained.

On modem dyeing units, the recommended dyeing temperature of 140°F (60°C) can be set within tolerances of about +2*C. The new dyes produce comparable results even at significantly larger temperature differences

"Normal" variations in the salt concentration are defined as -lO%, i.e. if the recommended salt concentration is 50 g/l, the concentration can vary from 45-55 g/l. Dyeings with the new dyes are relatively insensitive to even larger variations. The diagram shows a range of 40-60 g/l.

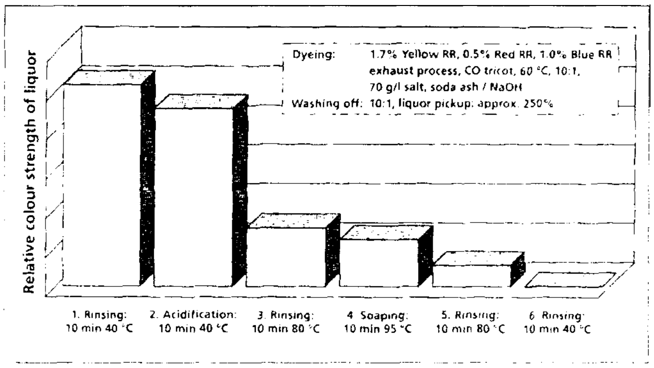
The same applies to variations in the liquor ratio, i.e. between 7:l and 13:l. High yields are obtained even if dyeings are produced at higher liquor ratios, as is common for example for polyester/cellulosic blends.

Nearly all major machine manufacturers now have units for dyeing at short liquor ratios. Investment in such units pays off because it cuts operating costs (energy, water, chemicals, dyes, etc.) and raises productivity by reducing processing times. Consequently, the aim should be to dye at the shortest possible liquor ratio.

The fixation yield obtained with the new dyes is roughly the same when using either soda ash/caustic solution or soda ash alone. Dyeings produced with these dyes do not change even if the dyeing time is prolonged considerably. This is important when adjusting the shade of dyeings or if unplanned dead times occur in manual dyeing processes because operators
are busy elsewhere.

These properties show that our trichromatic system is a convincing and cost-effective solution. Since success is not dependent on strict adherence to the dyeing parameters, the system enhances the reliability of dyeing processes and minimizes rejects.

Figure 6: Washing-off profile of a trichromatic dyeing with Remazol RR dyes.



Post rinsing

The affinity and diffusion behavior and the amount of unfixed dyestuff are the main factors affecting the cost of the washing-off processes. Optimum wetfastness can only be obtained if all unfixed dyestuff is removed from the fibers.

The high fixation yield of the new dyes means that only small amounts of unfixed dye need to be washed off. Figure 6 illustrates the washing-off process. Most of the unfixed dye is removed with the dye liquor when it is drained out of the bath. The first rinsing bath serves two main purposes: it reduces the salt concentration, thereby reducing the affinity of the unfixed dyestuff, and washes off the alkali. In the second bath, the goods are acidified to prevent partial hydrolysis of fixed dyes during the subsequent hot rinsing stage. The hot bath brings unfixed dyes to the surface of the fiber so that they can be washed off and removed when the wash liquor is drained from the bath.

Because of the low quantity of unfixed dye and the good washing-off properties of these dyes, post rinsing to obtain the required level of wetfastness can be performed quickly and requires relatively little energy and water.

In summary, the dyeing and post rinsing processes show that the new trichromatic system enables dyers to achieve dyeing times and a level of reliability that set new standards for reactive dyeing.

Fastness properties

With these dyes it is possible to obtain fastness properties that exceed the demands normally made on sports and leisure wear. Two features of the combination's fastness properties are outlined below.

Lightfastness

The three new dyes fade at essentially the same rate when exposed to light. The result is a lightening of the shade without a change in shade. On the other hand, should the blue dye in the trichromatic combination be replaced with a blue dye with higher lightfastness such as C.I. Reactive Blue 220, the dyeing will exhibit an objectionable change of shade after exposure to light.

Stability to acids

The dyestuff-fiber bond formed by the new dyes is extremely stable to acids, so these dyes are ideal for dyeing polyester/cellulosic blends by the reverse dyeing process (pre-dyeing of the cellulosic component followed by acidified overdyeing of the polyester component).

Effect of globalization

In recent years, the globalization of the market has had a major impact on competitive structures. Cost, quality and flexibility are now principal criteria for market success.

Dyeing Unmodified...
[Continued from page 18]

dyeings? Is the fastness to light, washing, crocking, dry cleaning, etc. good enough for commercial consumer products? Can the process be extended to dyeing polypropylene carpets? At this point, no continued work is being supported at The University of Georgia in this area, and it is unlikely that additional work will be done unless there is an expression of interest in this work and support of this work by industry. ❑

References

(1) Samanta, A. K. and Sharma, D. N., Dyeing of Polypropylene with some Azo Disperse Dyes of Basic Character via Chlorination Route, *Indian* Journal *of Fibre &* Textile *Research,* 20. No. 4, December 1995, 206.

(2) Akrman, J. and Kaplanova, M., The Coloration of Polypropylene Fibres with Acid Dyes, *Journal of the Society of Dyers and Colourists.* 111, No. 5, May 1995, p159.

(3) Prchal, V., Marcincin, A., Kristofic, M. and Ondrejmiska, K., Dyeing and Colourist Properties of Polypropylene Fibres, *Vlakna a* Texfil. 3, No. 1, January 1994, ~136.

(4) Prchal, V., Havllnova, B., Hodul, P., and Marcincln, A., The Zeta Potential of Polypropylene Fibres Modified by Nylons, *Vlakna* a Texti/, 2, No. 1, January 1995, ~*71.*

(5) Ondrejmiska, K, Recent Trends in Dyeing of Synthetic Fibres, *Vlakna a Textil, 1,* No. 1, January 1994, pll.

(6) Fulmer, T. D., Upholstery Sector More Demanding, *America's Textiles International,* 23, No. 1, January 1994, p76.

(7) Mansfield, R. G., Polypropylene Use in Apparel Grows, *America's Textiles International,* 23, No. 1, January 1994, P(K/A)8.

(8) Shukla, S. R. and Athalye, A. f?., Ultraviolet Radiation-Induced Graph Copolymerization of 2-Hydroxyethylmethacrylate onto Polypropylene, *Journal of Applied Polymer Science, 51, No. 9,* February 1994, p1567.

(9) Jambrich, M. and Durcova, O., Fibers from Polypropylene/Polyamide 6 Blend, *Fibers & Textiles in Eastern Europe,* 1, No. 1, January/February 1993, p34.

(10) Dayioglu, H., Polymeric Dye Receptors for Disperse-Dyeable Polypropylene Fibres, *Journal of Applied Polymer* Science, 46, No. 9, November 1992, p1539.

(11) Feng, Z., Icherenska, M., and Ranby, B., Photoinitiated Surface Grafting of Synthetic Fibers. IV. Applications of Textile Dyes onto Surface-Photographted Synthetic Fibres, *Angewandte Makromolekulare Chemie,* 199, No. 8, August 1992, p33.

(12) Herlinger, H., Augenstein, G., and Einsele, U., Innovative Methods for the Dyeing of Polypropylene. Il. The Influence of the Dyestuff Constitution and Auxiliaries, *Melliand Textilberichte,* 73, No. 9, September 1992, p737.

(13) Gawish, S. M., Kantouch, A., El Naggar, A. M.. and Mosleh, S., Grafting of 2-(dimethylamino) ethyl Methacrylate onto Gamma-Irradiated Polypropylene Fabric. *Journal of Applied Polymer Science, 44, No.* 9, March 1992, ~p1671.

(14) Stefanik, P. and Lesny, M., Dyeable Modified Polypropylene Bulked Continuous Filament Yarns, *Chemiefasern/Textil/industrie,* 41/93, No. 10, October 1991, P1173.

(15) Einsele, U., New Methods for the dyeing of Polypropylene. First Report: Dyeing with the Aid of Binders, *Melliand Textilberichte,* 72, No. 10, October 1991, p847.

(16) Baughman, G. L. and Perenich, T. A., Fate of Dyes in Aquatic Systems: I. Solubility and Partitioning of Some Hydrophobic Dyes and Related Compounds, *Environmental Toxicology and Chemistry, 7,* No. 3, March 1987, p183.

(17) Ahmed, M., *Polypropylene Fibers - Science and Technology,* Elsevier Scientific Publishing Company, New York, (1982) p462.

(18) Shore, J., "Dyeing of Polyolefin and Vinyl Fibres," in *The Dyeing of Synthetic-Polymer and Acetafe Fibres,* (D. M. Nunn, Editor), Dyers Company Publications Trust, Bradford, (1979), p392.

(19) Bird, C. L. and Patel, A. M., The Dyeing of Unmodified Polypropylene with Disperse Dyes, *Journal of the Society of Dyers and Colourists, 84, No.* 11, November 1968, p560.