Efficient Precipitation-Free Pre-Reduction Technique and Its Industrial-Scale Application to Enhance Color Strength of Vat Dyes

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Abstract: - An energy-efficient process, enabled via introduction of a new compact apparatus with low running-cost into the standard continuous textile dyeing process for production of deeply shaded yarns and fabrics of different colors is presented. High quality deep-shade effect is achieved by improved reduction efficiency of the used dye which is in turn proportional to the dye concentration in feed. However increased dye concentration in feed leads to severe precipitation problems making it practically impossible to transport the chemicals in order to run a continuous dyeing system. Therefore in the new process addressing this problem, chemical composition is introduced to the apparatus, namely the moderate-concentration precipitation-free pre-reducer (MCPR), which reduces the vat dye while transferring the chemicals from the individual sources to the point where they join the overall circulation, avoiding the aforementioned issues. The dye concentration within the MCPR is lower than that of feeding dye, allowing precipitation-free operation and is pronouncedly higher than that of the circulating dye, enabling dye reduction with significantly higher efficiency. Compactness is achieved via performing pre-reduction at high dye concentrations within a small-volume turbulent-flowing liquid, keeping the size of the apparatus and/or the whole system small and benefiting from the increased reaction rates known from the chemical kinetics. Efficient reduction performance renders it unnecessary to utilize costly high levels of heat and/or large amounts of reducing agents to increase the reduction probability of individual molecules as commonly practiced in prior art, leading to low running costs and to shorter reaction times required for the dyeing process.

Key-Words: - redox, pre-reduction, dye, vat dye, continuous dyeing system, textile, thread, denim

1 Introduction
This manuscript relates generally to the field of dyeing textiles to produce denim in continuous dyeing systems. More specifically, the proposal is related to increasing the dye reduction performance of the process via utilizing a peripheral unit namely the moderate-concentration precipitation-free pre-reducer (MCPR) to achieve higher color strengths in produced yarns and fabrics.

Denim is usually required to be dyed with ring effect, where the dye is around the fiber and does not penetrate radially into the center, so that visual effects can be build up on the final fabric. This requires low density pre-reduced dye to be picked up and to get oxidized on the fabric at multiple stages [1]. On the other hand, the color strength of the produced denim is desired to be as high as possible to produce deeply shaded colors and to provide the pattern designer with enough room or dynamic range for contrasts, requiring highly efficient dye reduction process [2, 3]. Considering the fact that dye reduction performance is proportional to the concentration of the unreduced dye, which conflicts with the former requirement, it becomes clear that these are two counteracting targets which are practically the main issues to be addressed in order to meet high demands of the denim industry.

Low density pre-reduced dye is easily achievable by the techniques known in the art [4, 5], however the process of vat dye reduction with high efficiency maintains its resistance in industrial applications. Dye reduction performance is proportional to the concentrations of both the dye in feed and the reducing agent, as the probability of reaction between them increases, leading to higher reduction ratios in the circulating liquor and thus to higher
color strengths of the final fabrics. However increasing the feeding dye concentration above a certain value leads to severe precipitation of the dye molecules making it practically impossible to transport the chemicals in order to run a continuous dyeing system. Considering the current state of the art, the latter issue is the bottleneck for high-capacity industrial plants.

2 Industrial Applicability Issues

Today the production of yarns with ring effect dyeing is feasible only through a few continuous processes. The most popular continuous processes used for dyeing yarns are rope (long chain) dyeing, slasher (sheet) dyeing, and loop dyeing (looptex). In these processes, indigo-derived vat dye is added in reduced form or in mixture with reducing agents to a dye tank [1, 6].

Indigo is a water insoluble organic substance that can be reduced to a water-soluble form and used to dye yarns or fabrics. Following dyeing, the dye is oxidized, which turns the dye into its water insoluble form on the yarn. Indigoid vat dyes have been primarily used for cotton yarns, which have given rise to the popularity of denim fabric today.

It is known, in the continuous dyeing of yarns, to add the dye in the form of a concentrated stock vat. A minimum of 2 dip-dye tanks is required for rope and slasher dyeing. Squeezing and skying takes place between the dipping steps and the dye is oxidized by air passage. To avoid dye depletion of the dip vats, the dye is replenished from stock vat dyes having a concentration greater than 80 g/l or at least 20% of the stock vat. These reduced stock vat dyes are introduced in the circulation line at the dye tank. The direct beam is recycled or looped several times in the same dip-dye tank. Fig. 1 shows continuous dyeing process for fabrics where “ready-to-dye” fabric is added to a series of dip dye tanks and squeezing/skying apparatus. The number of dip dye tanks, n, range preferably from 2 to 16 and they are accompanied by m squeezing/skying apparatuses. The n dip-dye tanks illustrated in Fig. 1 are connected in parallel via a circulation line. An example series/parallel combination configuration is when n dip-dye tanks are in a parallel configuration in the circulation line with respect to one another, while each tank is also connected in series via a leveling pipe. The circulation line may further comprise non-limiting additional elements, such as suction unit at end of each dip-dye tank, circulation pipe, circulation pump or other elements known in the art of dyeing textiles.

Similar to indigo, other vat dyes such as indigoid and anthraquinonoid as well have excellent all-round fastness properties on cotton. However, unlike indigo, most vat dyes have high molecular weight, substantivity, and low solubility. Hence, for most vat dyes no reduced stock solution is available off the shelf to use in denim fabric production. This fact forms the main issue this manuscript addresses.

It is desired to produce textile material with ring effect dyeing using various colors. However, the production of such textile material has been limited to vat dyes with high solubility, limiting the color range of denim fabric. Vat dyes, in particular anthraquinonoid vat dyes, have a wide range of colors, however most of these chemicals have low solubility.

Some of the attempts reported in the literature, uses dye dispersion instead of stock vat to solve the problem of supersaturation and insufficient concentration of stock vat. However, in these solutions, the circulating concentration of the dye is usually as low as 50:1 from stock vat to circulating dye, resulting in low dye reduction rate. It is known that the vatting rate is a function of the dye and the reducing agent concentrations. Therefore the prior art requires circulating liquor which is a slow process leading to low dye loading onto the final fabric. Increased unreduced dye in the circulating dip-dye tank results in poor dyeing, leading to poor rubbing and wash fastnesses.

Another remedy reported in the literature for the aforementioned issues is to use small baths, high heat and large amounts of reducing agents. However
under these conditions, the dye molecules can go some side reactions such as but not limited to over-reduction, dehalogenation, hydrolysis of the dyestuffs and high consumption of stabilizer chemicals due to the fact that the reducing agent can decompose at higher temperatures. In these processes the textile material is dyed from dry-to-wet where the dye pickup is intrinsically high without possibly a ring effect, an undesired result. Therefore we would like to have a system where the fabric is dyed wet-to-wet and at room temperatures.

3 Architecture of the MCPR Apparatus

Explained in details within the scope of this manuscript, we propose to add a new apparatus, as seen conceptually in Fig. 2, which allows all vat dyes to be used individually or in combination with other dyes in a continuous dyeing process for production of yarn or fabric with ring effect. Vat dyes are introduced to a treatment unit comprised of at least one reaction unit (MCPR) where the reducing agent is added to a mixture comprising a dye composition, caustic soda and/or other components or additives known in the art of textile dyeing. The dye concentration in the reaction unit is lower than that of feeding dye such that the severe problem of dye precipitation does not occur. However it is significantly higher than that of the circulating dye so that the dye is reduced efficiently. Although the preferred location for the MCPR is before the circulation line, any location before the dip-dye tank can be utilized without the aforementioned problem of slow reduction.

The pre-reduction is performed within a significantly small volume which is a few orders of magnitude less than that of the circulation system, leading to reduced running costs due to shortened reaction times, and to decreased heat and/or chemical consumptions.

MCPR has at least one reaction unit where unreduced dye composition, caustic soda, and reducing agent are mixed right before the reaction starts. MCPR has a retention time (RT) that is a function of reaction volume, flow rate, and mixing parameters. Each vat dye requires a different RT depending on the dye half-life, its solubility, and other chemical properties. In case a mixture of vat dyes is used, the properties of the least soluble or mixture may be used for RT design.

MCPR may have several reaction tanks in parallel equipped with contact thermometers, flow rate and various controllers to measure physical parameters. This enables the fine tuning of the dyeing liquor which may contain a variety of chemical compositions such as but not limited to dyes, reducing agents, and additives, wherein each composition has a different half-life, solubility and other chemical properties effective in dyeing process. MCPR allows further inclusion of milling and/or an ultra-sound apparatuses to treat individual components and to avoid aggregation problems independently before they start reacting.

The MCPR may have several parallel reaction units. Each reaction unit may have a different RT and/or temperature. This configuration provides for use of vat dyes of different solubility in a continuous process. Each reaction unit may be specifically designed for a particular vat dye based on RT, temperature, or other parameters to control reaction rate in order to achieve a desired reduced dye composition. Alternatively, it may be desired to reach a specific ratio of reduced to unreduced dye. The RT and temperature maybe adjusted to achieve any desired ratio of reduced to unreduced dye. The RT is adjustable via flow rate and the geometry of the reaction tank, temperature is dependent on the dye and the reducing agent, dyeing temperatures are usually in-between 20°C to 90°C, preferably confined to the range of 35°C-45°C in majority of industrial applications.

4 Measurement Results

The measurement results given in Fig. 3 shows a linear dependency of the color strength on initial dye concentration. This is the main proof of concept that it is practically possible to enhance the color strength of the final fabric by approximately 43% by employing the invention within a standard continuous dyeing system. This means that a system with less number of stages is enough to achieve a given target color strength or in other words, deeper
shades become available with fixed number of stages in a continuous dyeing system. Additionally, well defined concentration-to-color-strength gain of 0.76 %/g/l provides fine tunability. Thanks to the efficient pre-reduction performed within a small volume compared to that of the circulating system, the time required for the dye preparation phase is significantly reduced.

Fig. 4 shows the dependence of color strength on the fiber diameter for four independent experiments with different dyeing strengths expressed in terms of on-the-weight-of-fabric (OWF). All experiments show that color strength increases as the fiber size increases. This is expected because given the surface chemistry of the fiber and the type of dye molecules, increased fiber diameter means decreased total surface area which in turn mean that the number of dye molecules per unit area also increases, leading to darker shades on the surface.

5 Conclusions
We presented a method of utilizing the principles of chemical kinetics and collision dynamics, which allow reactions at low temperatures, and of using lower concentrations of reducing agents, which minimizes problems such as over-reduction, dehalogenation and hydrolysis, leading to an environment-friendly dyeing process.

In the proposed architectural modification to the standard textile dyeing technique, we establish the reaction control by molecular kinetics within the MCPR apparatus where the control parameter is neither the temperature nor the concentration of reactants. As a result, the contribution of our technique is in the way high concentration of indigo dye liquor is achieved.

We proposed a novel additional apparatus to all conventional continuous dyeing processes of textiles with vat dyes, independent of their poor solubility at high concentrations. The proposed apparatus is an interface between the dye stocks and the dye bath, which is applicable for a wide variety of vat dyes. Eventually, the apparatus together with the technique it allows is a tool-box for the textile dyeing industry which provides experts with the following additional advantages: small form factor of the apparatus, tunability of color strength, low running costs, higher processing speeds and reproduction precision [6].

References: