Textile Processes: from Wet to Dry
Part 1: Water saving and water-free dyeing and finishing treatments

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1. Introduction

Water is for the pretreatment, dyeing and post treatment of the textile the process medium. Under pressure from the growing environmental awareness and the measures taken by the different governments, the cost of water has increased and the availability is reduced. Finishing companies are forced to rationalize and to reduce the water and consumption. The implementation of textile dyeing machines with lower bath ratio’s, the minimization of water and energy use, the reuse of process water, including energy (heat), closed water cycles, improved efficiency of distribution systems, recovery of raw materials from waste water (for example salt in dyeing processes) or use of alternative water resources (rain and sea water) therefore are an economic necessity. However, for many SMEs, the investment is often too large to reuse the recycled water after an end-of-pipe technology and a more extensive purification of the total current. Up until now, reducing water consumption by selectively collection and reuse (without treatment) of some process streams appears only in a few cases possible. Using a logical frequency of the reuse of the baths also heat energy can be recycled!

This article discusses some sustainable technologies using less or no water to dye and treat textile materials. A few time ago the share of water cost in European textile industry was relatively low (6%), in other words the insensitive for change was not high enough or water was simply not of a major concern for our textile industry.

Today the textile industry as a whole is increasingly facing the ever-increasing scarcity of water and in some very tough challenges in meeting with stricter regulations that govern sustainable and environmental business practice. The textile industry being a major consumer and polluter of fresh water must address this issue urgently and needs to develop more sustainable production concepts. Innovative solutions for water-related challenges must result in creating market opportunities for European industry and SMEs.

Moreover, today the textile industry is experiencing severe shortages and tremendous price rise for the necessary raw materials to our production to the extent that it hampers extensively the competitiveness of our industry. The reduction and recycling/reuse of dyestuff are a high priority due to the actual high dyestuff prices (increase with more than 80% during the last months). The recent shutdown of chemical companies in China and India caused a sharp decrease in production of the main chemical intermediates going to the formulation of dyestuffs. Alternative supply from other countries is limited as those two countries have driven-out competition.

In the near future, the demand for modified or novel coloration technologies, waterless dyeing and recycling dyeing methods will increase dramatically.

2. From wet to dry – What’s in a name?

Is dyeing without water or in a dry state possible? Or can we eliminate hazardous wastewater as byproduct of dyeing textile? Today two processes fit to this picture, namely DyeCoo (abbreviation of CO2-dyeing) and Airdye® process (Colorep with Airdye Solution as partner).

2.1. SC-CO2 dyeing or dyeing without water

Problems associated with usage of water as dyeing/finishing medium are the high quantities needed per kg textile (often > 100 l/kg), effluent generation and additional step needed to dry the fabrics
after each step. The amount of energy spent during dyeing, rinsing spent to remove the water is also huge adding making processing often the weakest link among the entire textile chain. The unspent dyestuffs remain in liquor, thus polluting the effluent resulting in an additional pollution of waste water.
To eliminate the disadvantages it was proposed that certain gases can replace water as solvating medium. High pressure and temperature are needed to dissolve the dyes. Of all the gases being possible to convert into super critical fluids, CO₂ is the most versatile and prominently. Because of its high diffusion rates and low viscosities allow the dye to penetrate into the fibre. For the last three decades, supercritical fluids, which are characterized by exceptional physical-chemical properties, have been used in extraction processes (to extract natural substances for the production of drugs, cosmetics and spices).
For the textile industry waterless dyeing concepts such as dyeing of polyester fibres from supercritical carbon dioxide (sc-CO₂) are of major interest. However, the sc-CO₂ technology as such is not new. Sc-CO₂ dyeing has been pioneered by German universities (Schollmeyer et.al) more than 25 years ago. Several significant patents have been filed since 1988. CO₂-dyeing was and is still used for dyeing small narrow fabrics, sewing threads and hook-fasteners. A few CO₂-dyeing machines (Jasper – 1991- and Uhde Hochdrucktechnik – 1995- with its 30 l autoclave) have been introduced on industrial scale. Implementation partners were Germany based textile companies Amann & Söhne on polyester thread years, Ado Gardinenwerke and TAG Garne Teppichverdelung.
Due to lack of public funding and immense technological and financial obstacles to be overcome during scale up of the technology, industrial bulk scale for fabrics became only recently available. Now, 25 years after the invention and pioneer work, the Dutch company DyeCoo started entering the market. Strategic partnerships were set up with big brands such as Nike (read Nike-DyeCoo, the fabrics are marketed under the brand DryDye™ for their waterless dyeing technologies) and Adidas (Drydye range of T-shirts).
New industrial CO₂-dyeing machines became available for fabrics. Recently Huntsman Textile Effects and DyeCoo Textile Systems have signed a collaborative agreement on Supercritical CO₂ water-free Dyeing and finishing products. Supported by their partners Setex, Triade (dye distributor), FeyeCon (parent company) and Yeh Group the machine has been implemented at production scale at Tong Siang’s plant in Thailand.. According to ing. P. Decorte (CEO Tong Siang) the annual production is about

![Figure 1: industrial sc-CO2 dyeing machines (DyeCOO)](image)

**2.1.1. CO₂ as supercritical fluid**

CO₂ is a naturally occurring gas and it is virtually inexhaustible resource (atmosphere, combustion processes, and natural geologic deposits) and readily available for industrial consumption. Other attributes are: chemically inert, physiologically compatible, relatively inexpensive, non-toxic, non-hazardous, non-flammable and non-corrosive. In addition it has no disposal problems.
Furthermore pressures of 260 bar require a special design of the textile machinery and upscaling requires a very significant investment. Furthermore pressures of 260-280 bar - in contrast to a few bars in conventional HT-dyeing - may

Any gas above its critical temperature retains the free mobility of the gaseous state but with increasing pressure its density will increase towards that of a liquid. The properties, which are intermediate between gases and liquids are controlled by pressure.

Carbon dioxide is the most investigated and used gas in the supercritical fluid dyeing process. It is a naturally occurring, chemically inert, physiologically compatible, relatively inexpensive and readily available for industrial consumption. Figure 2 shows that above 73 bar and 31°C carbon dioxide becomes a supercritical fluid meaning that carbon dioxide has valuable properties of both a liquid and a gas, liquid-like densities and gas-like low viscosities and diffusion properties, resulting in improved mass transfer. This helps in dissolving non-polar dyestuffs (read: disperse dyes) as well as in shortening dyeing cycles.

2.1.2. Sc-CO₂ dyeing machine

The apparatus (figure 3) used for dyeing with supercritical sc-CO₂ consists of a temperature controller, a stainless steel dyeing vessel, a heater that surrounds the vessel, a manometer (an instrument for measuring the pressure of a fluid), a carbon dioxide pump and a cooler for cooling the head of the carbon dioxide pump. The high pressures used during dyeing (260-280 bar) require a special design of the textile machinery and upscaling requires a very significant investment.
also cause mental restrictions.

2.1.3. Sc-CO₂ dyeing – practice

There are three components in the supercritical CO₂ dyeing process: the CO₂ gas, disperse dyestuff (pure, without auxiliaries such as levelling and dispersing agents) and fiber polymer. The dyeing is carried out at 260-280 bar and 130 °C during ca. 2 hours.

During the dyeing of polymer fibers, CO₂ loaded with dyestuff penetrates deep into the pore and capillary structure of fibers. This deep penetration provides effective coloration of the intrinsically hydrophobic materials. The process of dyeing and the removing the excess, non-fixed dye (< 5%) are carried out in the same plant. A further advantage of this dyeing technique is that the excess dye can be easily separated from CO₂ and can therefore be recycled/re-used. Also CO₂ is fully recovered from the process in the form of an uncontaminated gas and can be reused.

There are a large number of advantages inherently linked to sc-CO₂ dyeing of PES are summarized in table 1. Experience with bulk to bulk reproducibility and fastness levels are claimed positive. Moreover in a very competitive global textile industry, sc-CO₂ dyeing is a marketing tool for brands such as Nike, Adidas as well as for processing houses to be able to manufacture in a green process and on the demand of environmentally conscious customizer for sustainable products.

One of the main problems and obstacles is the high cost of the dyeing unit. One way of offsetting the capital cost could be for supercritical CO₂ to be extended to include pre-treatments such as sizing and desizing and posttreatments. However, this will not be easy. Furthermore, there are still challenges regarding equipment cost, equipment maintenance and the dyeing of other fibers. And what about the transfer from lab to industrial scale? Parameter dependency is reported to be quite high, meaning that there may be issues with lab-to-bulk and bulk-to-bulk repeatability, depending on the design of the machine and availability of a suitable lab scale equipment. Other problematic issues mentioned are oligomer migration and surface precipitation of dyes, resulting in non-appropriate fastness properties.

Table 1: SWOT analysis of sc-CO₂ dyeing
### Strength

- Operational costs < water dyeing (only 20% energy requirement compared to HT-PES dyeing)
- Dyeing time ca. 2 hours (compared to conventional dyeing/washing, drying times of 3-4 hours per batch)
- Full recycling, complete removal and recycling of CO₂ after processing without need for drying
- No consumption and discharge of waste water at all – dye remains as powder (compared to high volumes of waste water contaminated with residual dye chemicals etc.)
- New industry benchmark
- CO₂: inert medium (in contrast to water characterized by pH, hardness)
- Strip “off shade” batches

### Weakness

- Currently limited to PES dyeing
- Cleaning process of dyeing unit
- Work in progress...
  - Operational knowhow
  - RFT factors
- High investment cost reaming an obstacle

### Opportunity

- Green field investment
  - @ needle point
  - @ point of sales
- Cost gap will widen
- Capacity growth without waste water restrictions
- DryDye™ V 2.0 will outperform current technology

### Threats

- Stronger collaboration needed:
- No availability of finishing chemicals
- No availability of dyes for other fibres
- Green washing

#### 2.1.5. Sc-CO₂ dyeing of other fibres?

So far the technology is a commercially viable system for dyeing polyester, and to a lesser extent elastane and nylon. However, the colour buildup of disperse dyes is for PA and elastane fibres limited and there are still certain hurdles which need to be overcome before the system can be used on a large scale. At present, the dyeing of natural fibres (cotton, wool etc.) using common conventional dyes doesn’t work mainly because of solubility issues of these dyes in sc-CO₂ and swelling issues (no swelling of polar fibres in sc-CO₂). Attempts to overcome these problems by pre-treatment using swelling agents would be needed however this demands for additional processing steps (for pre-treatment and washing) talking away the advantages of water less dyeing. Another attempt is the use of reactive disperse dyes (disperse dyes with built-in reactive MCT-groups, without water solubilising groups) were made and published. Even if the dyeing was successful the question remains: which chemical company will carry the investments for development, registration (Reach) for a ‘niche’ technology?

#### 2.2. ‘Sublimation dyeing’ - AirDye®

Today, an American company AirDye® (with Colorep as partner) introduce an dyeing process using air instead of water. The process is based on the well know sublimation or transfer technology from the
printing industry using disperse dyes and special chemicals. AirDye® technology features a one-step process that bypasses the liquid state of dye altogether. The company claims that depending on the fabric, and type of dyeing its new dyeing process uses up to 95% less water, and up to 85 % less energy, contributing 84% less to global warming.

Proprietary disperse dyes (Sibius™ disperse dyes) are transferred from paper onto fabric using heat, without consuming water or emitting pollutants. The transfer paper is recycled, and used dyes and toners are also recycled to make tar and asphalt.

AirDye® operates and licenses patented textile printing machines that colour one or both sides of the fabric simultaneously, and with independent colour control. No water is used in this process, and no post-treatment or finishing is required. Unlike traditional heat transfer printing, the AirDye® process is 2-sided without negative impact on the hand feel of the finished fabric is luxurious and clean. The flexibility of the process gives the designers more creative freedom. Unlike rotary screen wet printing, it is possible to independently colour each side of the fabric, and no water is used in the dyeing or finishing. This process creates new design capabilities, including the ability to contrast (or match) two sides of the same fabric, with solids or prints.

It can be used on fabrics (interior, apparel, promotional textile) as well as on T-shirts. The flexibility and short leadtime of the technology give the freedom of wait longer to decide what colour or print to put onto their fabric, which would reduce the need for apparel makers to guess what colours consumers will want to wear months ahead.

3. Other water-saving technologies for garments

On garments, in particular jeans the use of ozone technology slashes the use of water, energy and chemicals. The technology allows companies such as AG Adriano Goldschied, USA to clean up the excess indigo without the use of large amounts of water and pocket-whitening chemicals to rid of the dyestuff.

Also the Spanish company Jeanologia, specialised in garment finishing, also use ozone rather than multiple washes to fade its denim. The company claims it saves nearly 15 million of water daily across its facilities worldwide.

The same company developed the E-flow or Zero discharge technology for garment treatments. In this new technology air from the atmosphere is transformed into nanobubbles. Products and water then naturally distribute themselves forming the nanobubble skin, making a perfectly homogeneous mix between water, products and air.

The skin of the nanobubbles is responsible of transporting the properties of the product to the garment in an optimal & efficient way. Focus is on the softening, water repellence finishes and resins for 3D-effects.
will be followed …

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To be followed…

(Article based on information from Dyecoo, Colorep, Airdye, Nike, Adriano Goldschied, C. Schumacher, Schollmeyer et all, Jeanologia and ing. P. Decorte (CEO Tong Siang, UNITEX-mini-symposium ‘Sc-CO₂ dyeing: Utopia or reality, Gent - 11.06.2014)