Waterless Dyeing Technology

Smart Manufacturing and Materials Division



- Textile industry is one of the biggest consumers of water
 - On average, an estimated 100–150 liters of water are needed to process 1 kg of textile material
 - In garment manufacturing, about 50% of waste water comes from textile dyeing and finishing processes









Country Regulations

List of selected countries that have a prominent textile industry and if regulations were identified.

	Country	Obtained a wastewater regulation with effluent values
1	Bangladesh	Yes (T)
2	Brazil	Yes
3	Cambodia	Yes
4	China	Yes (T)
5	Honduras	•
6	India	Yes (T)
7	Indonesia	Yes (T)
8	Malaysia	Yes (T)
9	South Korea	Yes
10	Taiwan	Yes (T)
11	Thailand	Yes (T)
12	Turkey	Yes (T)
13	Vietnam	Yes (T)
14	Sri Lanka	Yes (T)

Stringent control on pollutant discharge

The contaminated water must be treated prior to disposal or recycling

Water Ten Plan - Implications Across Target Industries

Target Industries	Compliance By 2016/17 or Shutdown		Strictly Control Projects Along 7 Key Rivers		Wastewater Reuse	Water Efficiency To Reach Advance Levels
Paper & Pulp	~	~		~	~	~
Coking	~	~				
Non-ferrous Metals		~	~	~		
Textile Dyeing & Finishing	~	~	~	~	~	~
Leather	~	~			~	
Nitrogen Fertiliser		~				
Pesticide	~	~				
Agriculture Food Production & Processing		~				
Pharmacy Production		~	~	~		

Source: China Water Risk, Water Pollution Prevention & Control Action Plan (Water Ten)



Notes:

(T) = Has values specific to the textile industry

* Does not have national regulation regarding industrial wastewater discharge

Source: Textile Industry Wastewater Discharge Quality Standards - ZDHC



! Rising costs of water and wastewater treatment



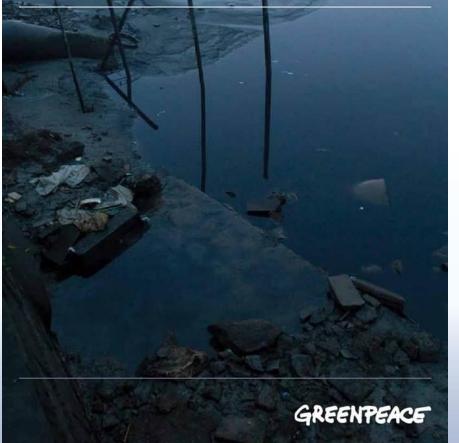






Dirty Laundry

Unravelling the corporate connections to toxic water pollution in China



WATER MATTERS DECISIONS TODAY FOR WATER TOMORROW

TODAY'S FIGHT FOR THE FUTURE OF FASHION

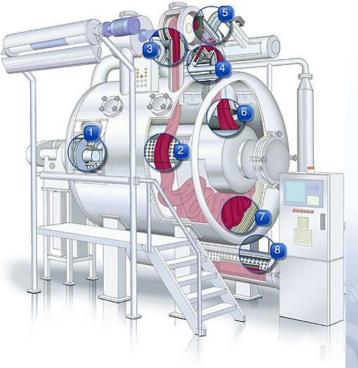
Is there room for fast fashion in a Beautiful China?

RISK

Water-Saving Solutions

- Air-Flow Dyeing Machine
 - > The fabric transport is carried out by air only, no dye liquor or aqueous medium is required to transport the fabric.
 - > A 53% reduction in water consumption.





Water-Saving Solutions

- AVITERA® SE Dyes
 - Poly-reactive dyes with three reactive groups for cotton and other cellulosic fibers
 - > Rapid and very high exhaustion
 - > High fixation (~90%)
 - Excellent solubility, high diffusion and outstanding washing-off properties, making them suitable for application at ultra-low liquor ratios.



Waterless/Nearly Waterless Dyeing

- I) Digital Printing
- II) Sublimation
- III) AirDye®
- IV) Supercritical Fluid Dyeing



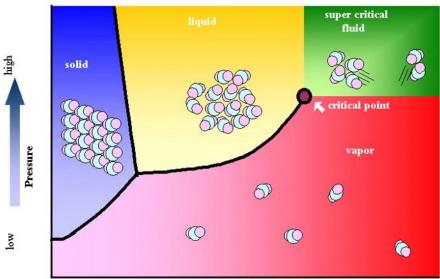




What is a Supercritical Fluid?

A supercritical fluid is any substance is any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist.

- It exhibits both the properties of a gas and a liquid.
 - Dense like a liquid to dissolve materials
 - Low viscosity, high diffusivity, no surface tension like a gas



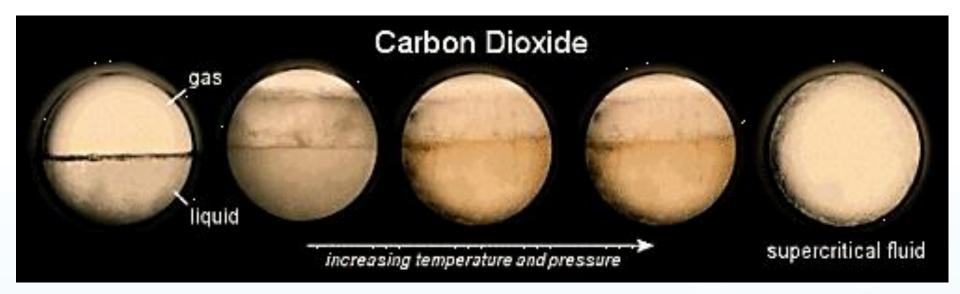
Temperature

Table 1. Order of magnitude comparison of physical properties substance*

State	Density [g/cc]	Viscosity [g/cm-s]	Diffusivity [cm ² /s]
Gas	0.001	10 ⁻¹	10-4
Supercritical fluid	0.1-1.0	10-4-10-3	10-4-10-3
Liquid	1.0	10 ⁻⁵	10-2



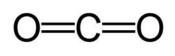
high





Green Solvent — Supercritical Carbon Dioxide

Carbon Dioxide (CO₂)





- > Non-toxic
- Non-flammable
- Non-corrosive
- > Does not contribute to smog
- No acute ecotoxicity

- Inexpensive
- Readily available
- Inexhaustible resource



Green Solvent – Supercritical Carbon Dioxide

However...

Carbon Dioxide (CO₂)



- ➤ A greenhouse gas → Global warming
- CO₂ concentration in the atmosphere increased from about 280 ppm in 1800 to 315 ppm in 1960, and since the mid-1900s, CO₂ levels have been continually increasing at an average annual rate of slightly more than 1 ppm. Nowadays the CO₂ concentration is about 380 ppm.
- Processes, which apply CO₂ as a solvent, do not increase CO₂ emissions, but rather provide an opportunity for recycling of waste CO₂.

3807 CO2 help

Supercritical Carbon Dioxide

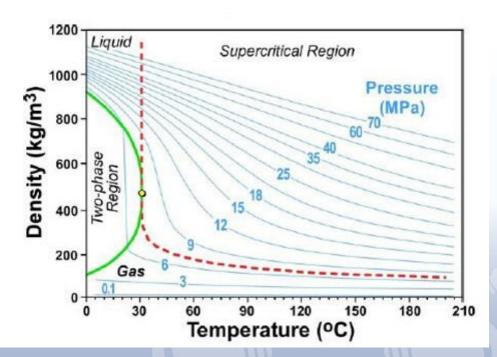
Critical Pressure (bar)	73.8
Critical Temperature (°C)	31.1
Critical Density (g/cm ³)	0.468

Tunable solvating power

- Tuning of solvent properties easily as a function of temperature and pressure.
 - → Can dissolve compounds of different chemical structures

A 'hybrid solvent'

 Can be tuned from liquid-like to gas-like without crossing a phase boundary



Applications

- Food industry
- Cosmetic industry
- Pharmaceutical industry
- Polymer and plastics industries
- Chemical industry
- Material industry
- Wood industry
- Textile industry

- Extraction
- Purification
- Sterilization
- Cleaning
- Micro- and nanoparticles synthesis
- Aerogel preparation
- ..



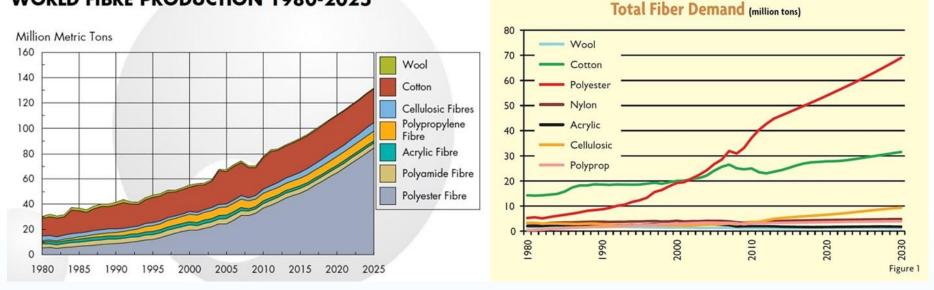
Supercritical Carbon Dioxide Dyeing

Historical Survey

- 1989 The first experiences of dyeing of PET in a high pressure phase equilibrium plant of 6 mL were made at Deutsches Textilforschungszentrum Nord-West e.V. (DTNW) and Prof. G M Schneider from the Ruhr-University of Bochum (Germany).
- 1990 A static dyeing apparatus consisting of a 400 mL autoclave with a stirrable, perforated dyeing beam was developed by DTNW.
- 1991 The first dyeing machine on a semi-technical scale with a volume of 67 L was constructed by Jasper GmbH & Co., Velen (Germany).
- 1995 UHDE Hochdrucktechnik GmbH, Hagen (Germany) and DTNW developed a new CO_2 dyeing pilot plant with an autoclave of 30 L, including an extraction cycle for removal and separation of excess dyes and for recycling of CO_2 .
- 2009 DyeCoo Textile Systems BV (Netherlands) launched the first commercial CO₂ dyeing machine with a volume of 200 L.



Polyester Fibers Continue To Grow

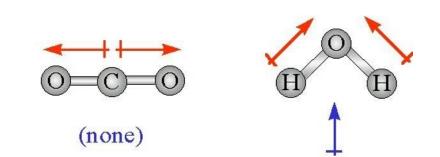


WORLD FIBRE PRODUCTION 1980-2025

- The production and demand of polyester have continued to grow at a significantly faster rate than all other fiber types
- Polyester makes up 95%+ of future global synthetic fibre production growth
- From 1980–2014, total fiber demand growth has been 40.7 million tons 73.4% of which is down to polyester

Supercritical Carbon Dioxide Dyeing

- Supercritical carbon dioxide (scCO₂)
 - Non-polar solvent the dipoles of the two bonds cancel one another
 - \rightarrow Direct dissolve of **disperse dyes**
- Disperse dyes



- Typically non-ionic and contain no strong hydrophilic (water loving) groups
- Dye particles are held in dispersion by surface-active agent (surfactant)
- Have substantivity for hydrophobic fibres, like polyester and acetate

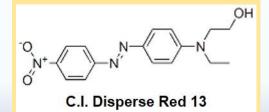




Chemical Structure of Disperse Dyes

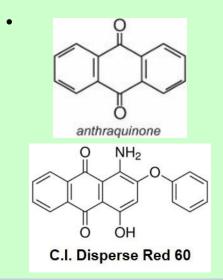
Azo Dyes

- Account for more than 50% of the total commercialized disperse dyes
- The characteristic feature is the presence in the structures of one or more azo groups, -N=N-



Anthraquinone Dyes

 A significant proportion (20%) of the disperse dyes



Others

- Nitroarylamino dyes
- Coumarin dyes
- Methine dyes
- Naphthostyryl dyes
- Quinophthalone dyes
- Formazan dyes
- Benzodifuranone dyes



Classes of Disperse dyes

Low Energy

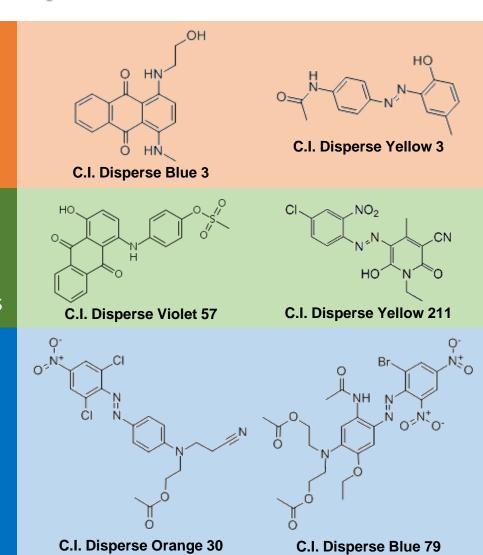
- low molecular weight
- high dyeing rate
- low sublimation fastness

Medium Energy

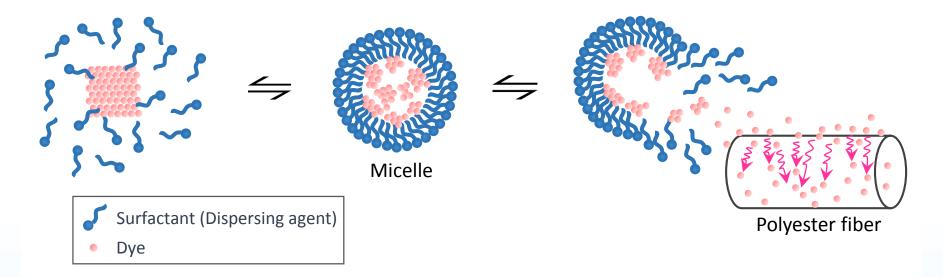
- moderate molecular weight
- moderate dyeing rate
- moderate sublimation fastness

High Energy

- high molecular weight
- low dyeing rate
- high sublimation fastness



Disperse Dyeing Mechanism



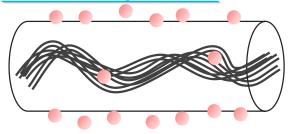
- 1) Some of the dyes dissolve in the water of the dyebath in the form of micelles with the aid of surfactant.
- 2) Molecules of dye are transferred from solution to the surface of the fibre.
- 3) The adsorbed dye diffuses monomolecularly into the fibre.



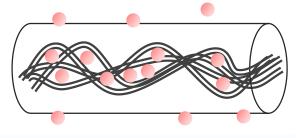
Disperse Dyeing Mechanism

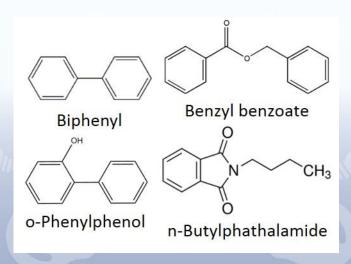
- Rate of dyeing depends on the rate of diffusion
 - Dyes of small molecular size have higher diffusion coefficients
 - The washing fastness is only fair
 - → Dyes of higher molecular weight provide adequate fastness
- To increase the dyeing rate and dye in deep shade
 - > Higher dyeing temperatures above 100°C
 - \rightarrow The swelling of fibre
 - Utilization of carriers
 - \rightarrow Increases affinity to polyester and swells it

At low temperature



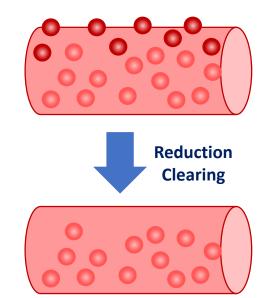




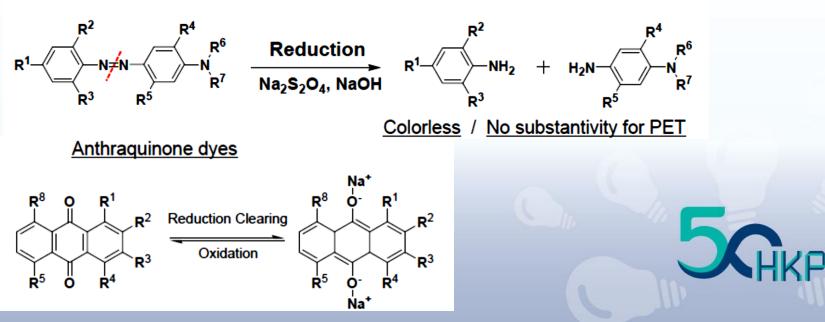


Reduction Clearing

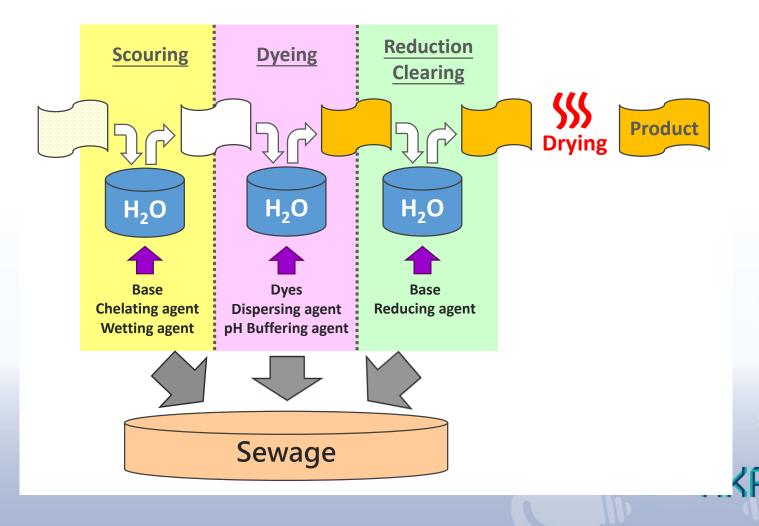
- To remove excess dye on the fiber surfaces
 - Improve wash, sublimation and crock fastness as well as the brightness of the shade
- The dyed fibre is treated in a strong reducing bath made up of sodium hydrosulfite (sodium dithionite, Na₂S₂O₄)and caustic soda (sodium hydroxide, NaOH)



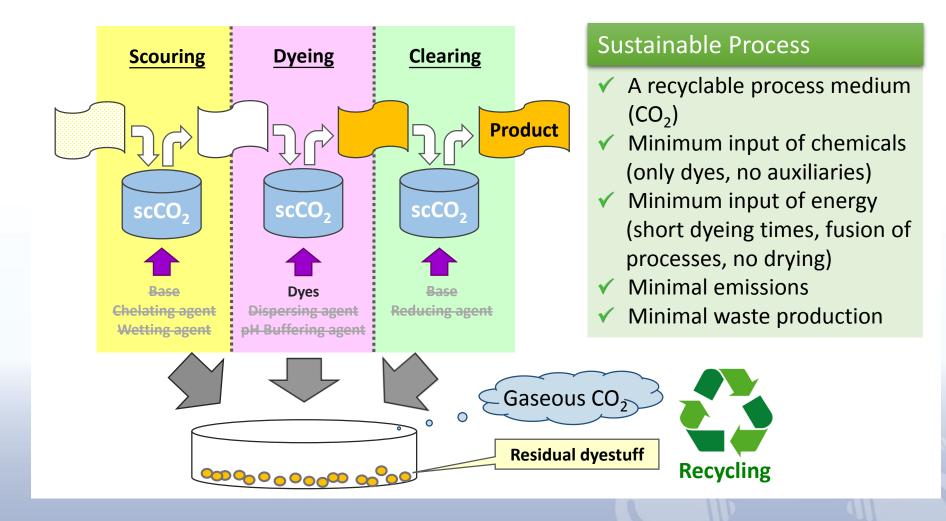
Azo dyes



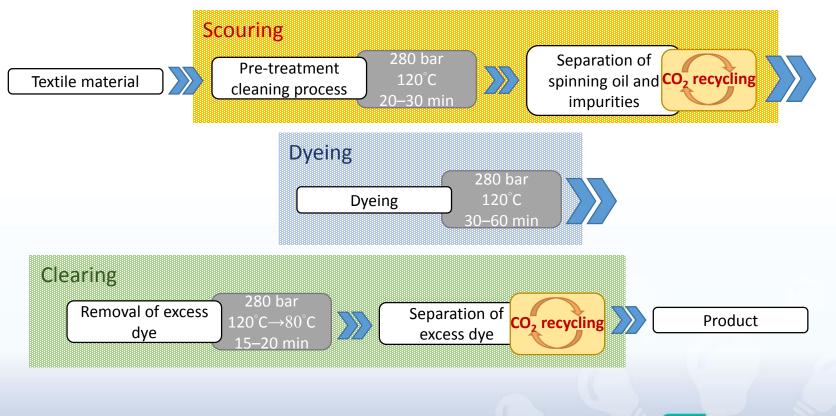
Conventional Water-Based Dyeing Process



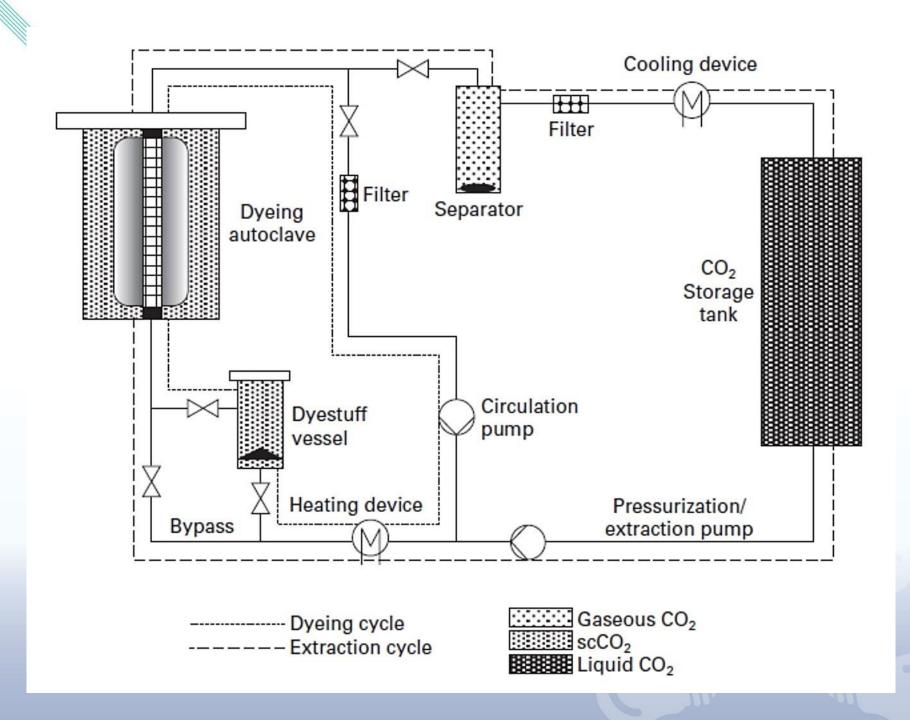
Supercritical Carbon Dioxide Dyeing Process



Supercritical Carbon Dioxide Dyeing Process





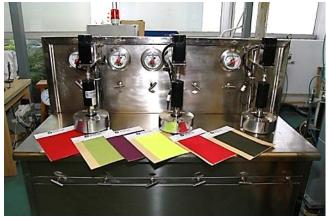


Supercritical Carbon Dioxide Dyeing Process





- ScCO₂ Dyeing Systems HKPC[©]
- Lab and pilot scale systems ٠





• Industrial scale systems





Processing Cauldron

Carbon Dioxide Storage Tanks

Pressurizing and Circulation Pumps

Chemical Addition and Separation Tanks

50HKPC

Temperature Control Units

Loading and Unloading Unit

Safety Components

System Control Unit





Processing Cauldron

- > Two processing cauldrons allow parallel processing
- > 500 L capacity
- > Process up to **2000 yards** of fabric
- Average daily capacity 30,000 yards
- > Equipped with a fully **automated hydraulic-door** with a double locking system



Carbon Dioxide Storage Tanks

Two CO₂ storage tanks store up to 12.5 m³ of CO₂



Carbon dioxide storage tank (2.5 m³)



Carbon dioxide storage tank (10 m³)

Pressurizing and Circulation Pumps

- Pressurizing pump with operating pressure up to 350 bar
- Circulation pump can deliver a continuous
 flow at a rate up to 50 m³/h
 - \rightarrow Integrated with an automated valve



Pressurizing Pump



Circulation Pump



Chemical Addition and Separation Tanks

- > External chemical addition tanks for easy addition of dyes/finishing agents
- Separation tank for easy recovery of residual chemicals



Separation Tank



Chemical Addition Tanks

Temperature Control Units

Heaters, chillers and heat exchangers





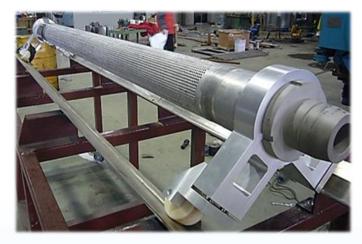






Loading and Unloading

Specially designed shaft and trolley for loading and unloading









Safety Concerns

- For textile finishing manufacturers, process conditions of up to 300 bar are very unusual
- Some mental reservations can possibly arise
 - Handling high pressure is not a problem because the machines are constructed in such a way so as to afford maximum safety levels for the operating staff
 - Withstand up to 350 bar (25% more than the normal operating pressure of 280 bar)



Safety Components

- Safety valves are installed at
 - Processing cauldrons
 - CO₂ storage tank
 - Chemical addition tanks
 - Separation tank
 - Pressurizing pump
 - CO₂ incoming pump









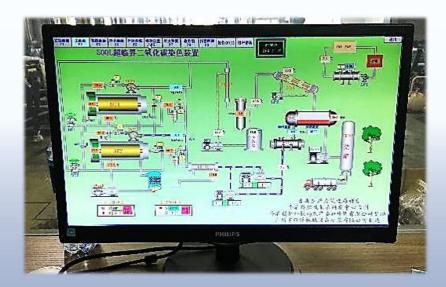






System Control

- > Custom made user friendly software with a process diagram view
 - \rightarrow Monitor and control the system
 - → Production parameters are recorded for reference and quality control
- Separated control room
 - → Remotely monitors and controls the system







Certification

Inspected and certificated by
 Jiaxing Special Equipment
 Inspection and Testing
 Institute

计量认证号 2015110883L	国家检验机构认可 检验: CNAS IB0125	检验检测机构核准证号 TS7110061-2016	
	申请编号	号: YA2015-497	
	报告编号	号: <u>DAF2015-0976</u>	1
压力	」 管道安装安 监督检验报		
工程名称:	嘉兴利维科技超临界染色	项目压力管道工程	1
建设单位:	三养纺织(嘉兴)有限公	ন	
监督检验单位:	嘉兴市特种设备检验核	金测院	
监督检验时间:	2015年12月10日 3	至 2016年01月20日	
ŝ	《兴市特种设备检验	检测院	

ScCO₂ Dyeing Systems





eco₂Dye

1 × 20L



Solubility of dyes

- Low dye solubility $[10^{-4} \text{ and } 10^{-7} \text{ mol dye/mol CO}_2]$
- Extensive grinding of the pure dyes enhances solubility
 - Increases of the surface area
- Molecular weight
- Dye structure
 - Solubility is decreased by the introduction of highly polar hydroxyethyl (–CH₂CH₂OH), amino (–NH₂), cyano (–CN), acetylamino (–NHCOCH₃) and carboxy (–COOH) groups
 - Halogen (Cl, Br, I, etc.) and nitro (–NO₂) groups have a positive effect on the solubility

Static system vs Dynamic system

- A static dyeing apparatus without CO₂ circulation
 - > Agglomeration, crystallization and melting of dyes \rightarrow lower solubility
- Takes 2-3 days to obtain dyeing equilibrium without CO₂ circulation

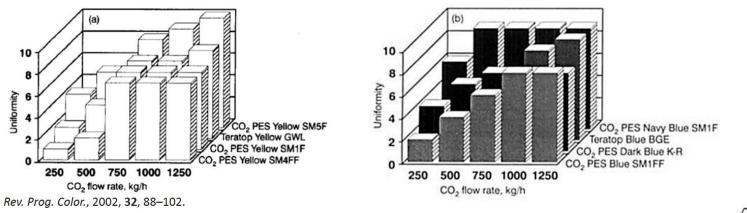
Quality of Dyeing

Dye distribution between the fibre and CO₂

- Dye exhaustion from the solution >> Sorption into the fibre.
 - > Precipitation of the dye on the fibre surface \rightarrow poor fastness properties

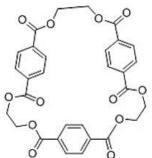
CO₂ flow rate

• Highest influence on the levelness



Cyclic trimers

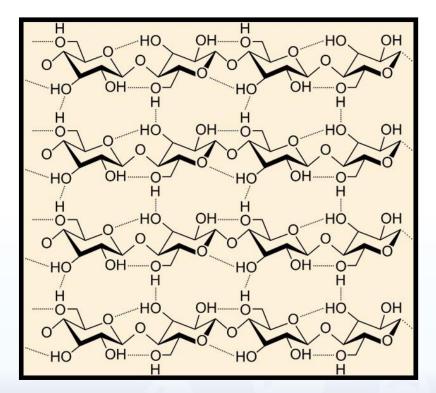
- Oligomers, mainly cyclic trimer, diffuse from the inside of the fibre to the surface
 - > Visual problems at dark shades and lower brilliancy of shade



Cotton has a market share of 37%

Problem of dyeing cotton in scCO₂

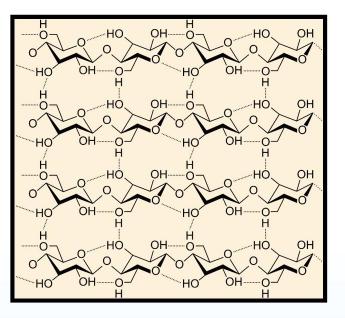
- Inability to break the highly hydrogenbonded cross-linking structure
 - Hindered the diffusion of dyes into the interior
- Disperse dyes only show slight interactions with cotton fibres
- Reactive dyes which are used in conventional water dyeing are nearly insoluble in scCO₂





Early attempts with disperse dyes...

- Impregnation of hydrogen bond-breaking substances
 - Swells the cotton fibre by breaking hydrogen bonds between cellulosic polymer chains
 - \rightarrow increase the accessibility of cellulose to the dyes



- The impregnation and the removal of the hydrogen bond-breaking substances has to be carried out by aqueous processes
- X Low wash fastness properties
 - Colour strength decreases remarkably after washing
 - > Weak interaction between cotton fibre and dyes



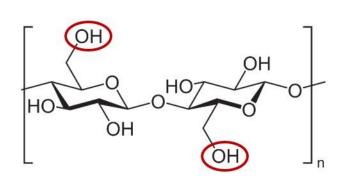
Fibre modification

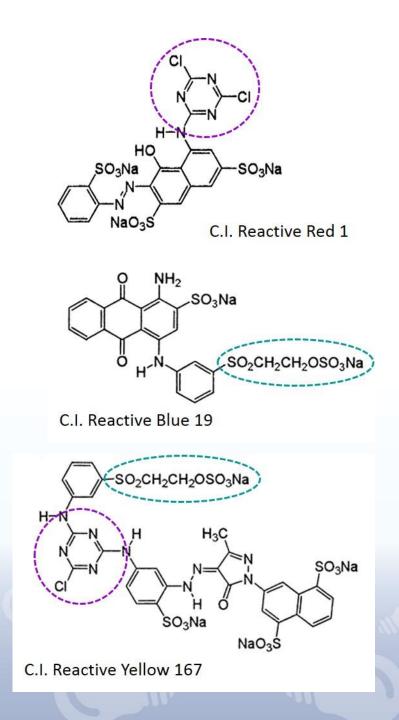
- Introduction of hydrophobic functional groups which can interact with disperse dyes
 - 1) Dicyclohexylcarbodiimide (15-20% owf) in chloroform
 - 2) Benzoylthioglycollate (BTG)
 - 3) Benzoyl chloride (22% owf)
- Pre-treatment and in some cases after-cleaning have to be carried out in water or other solvents
 - Require additional energy-consuming treatment and drying step
- ➤ High concentrations of the modifying agent are needed
 - Significant changes in the fibre properties



Reactive Dyes

- Soluble in water
- Containing reactive groups like chlorotriazine or vinyl sulphone groups
- Forms covalent bond with the fibre through the reaction with the hydroxyl groups of cellulose
- Polyfunctional dyes to improve fastness and/or fixation degree

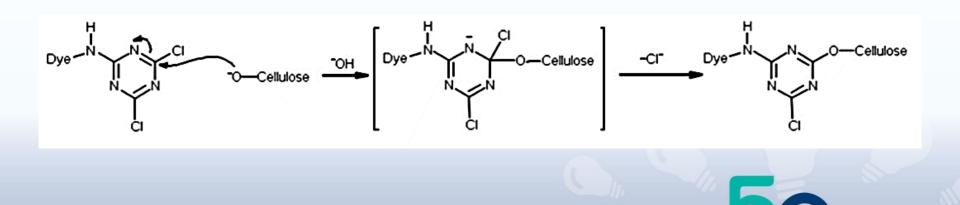




Reactive Dyeing Mechanism

Chlorotriazine type reactive dyes

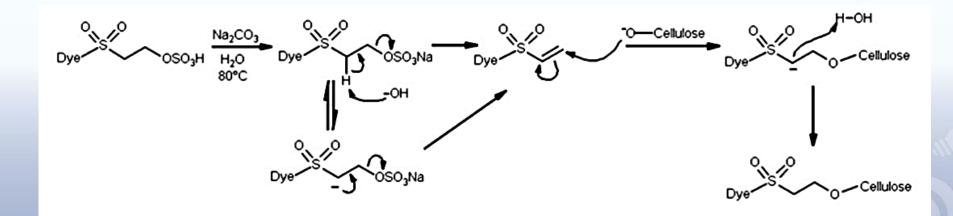
- Nucleophilic substitution (S_NAr)
 - 1) Nucleophile (the cellulosate anion) attacks at the carbon atom bearing the leaving group, i.e. chloride, to form a resonance-stabilized intermediate;
 - 2) The substitution reaction is completed by the elimination of the leaving group.



Reactive Dyeing Mechanism

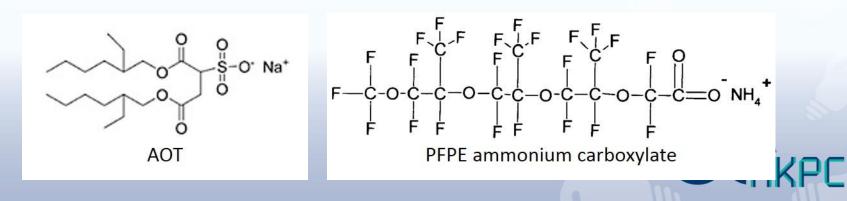
Vinyl sulphone type reactive dyes

- Nucleophilic addition
 - 1) Sulfatoethylsulphone group converses by an elimination reaction into the highly reactive vinyl sulphone group under alkaline conditions;
 - 2) The cellulosate anion attacks on the vinyl sulphone and leads to the a resonance-stabilized anionic intermediate;
 - 3) The addition reaction is completed by protonation.

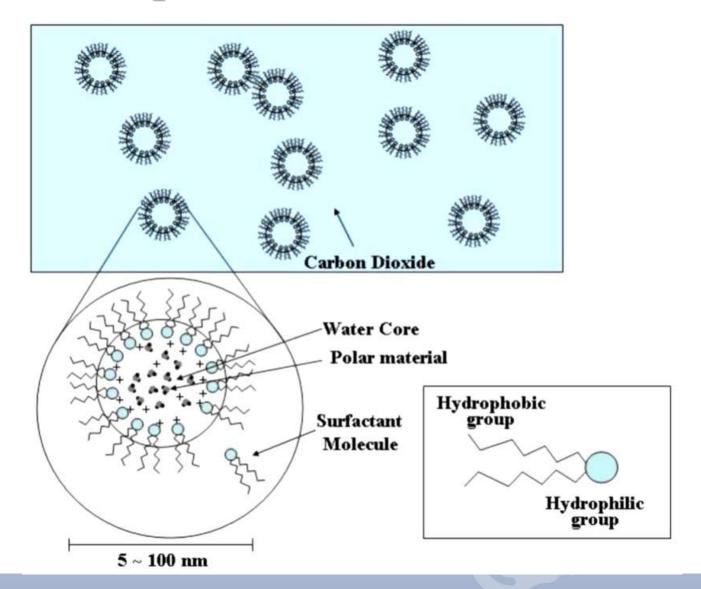


Use of co-solvents

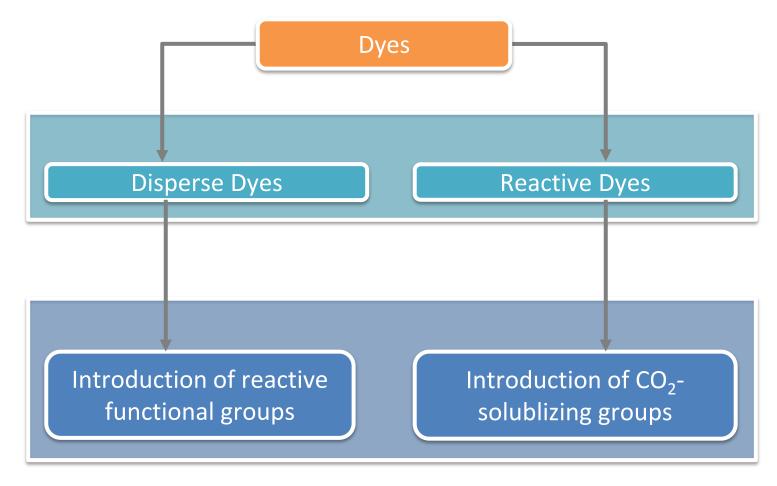
- Water or alcohols are the most important co-solvents
 - > To increase the polarity and the solvent power of carbon dioxide
- The solvent properties of scCO₂ can be vastly improved by the incorporation of surfactant
 - Surfactants, such as perfluoropolyether (PFPE) based and sodium bisethylhexyl sulfoccinate (AOT), etc., are amphiphilic molecules containing both a CO₂-phobic and a CO₂-philic portion



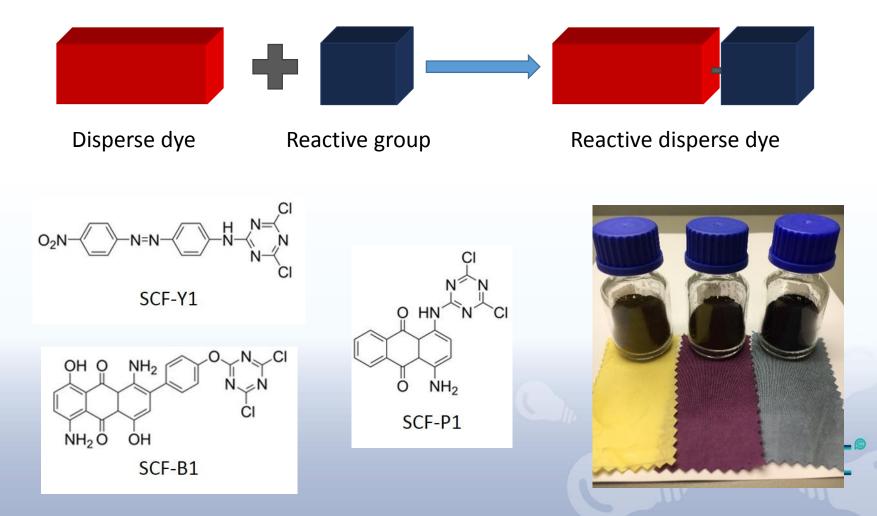
Water-in-CO₂ Microemulsions



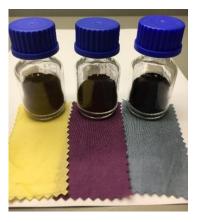
Development of CO₂-soluble dyes for cotton



Reactive disperse dyes



	Fastness		
Dye	Wash	Rub	
Reactive Disperse Yellow SCF-Y1	4–5	4–5	
Reactive Disperse Purple SCF-P1	4	4–5	
Reactive Disperse Blue SCF-B1	3–4	4–5	

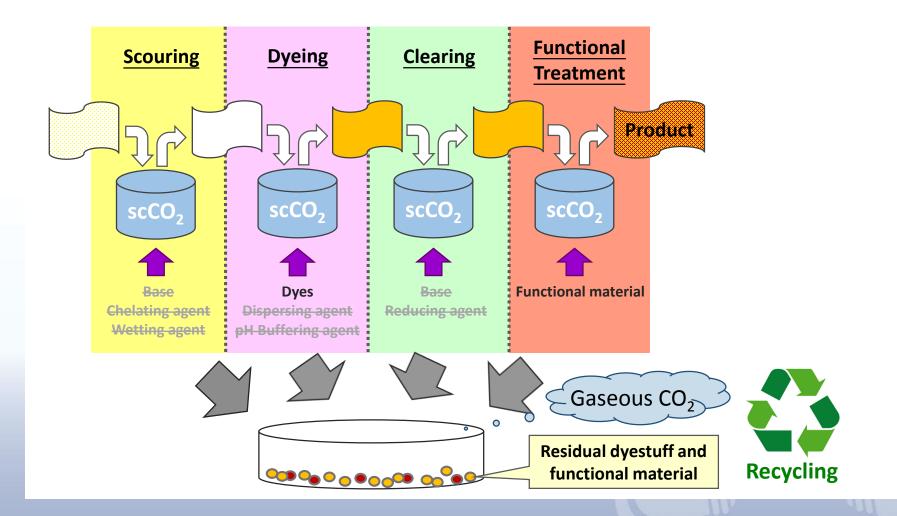


Poortivo group	Colourviold	Fastness		
Reactive group	Colour yield	Wash	Rub	Light
Trichlorotriazine (TCT)	Low	1,3,5	5	4
2-Bromoacrylic acid ester or amide (BAA)	Mid–High	4–5	5	5
Vinyl sulphone	Mid–High	1–2	4–5	1–2

- Highly corrosive hydrochloric acid from TCT and hydrobromic acid from BAA are released
 - > Damages the fibre as well as the machinery equipment



Integration of Functional Treatment Process



Economic Evaluation of scCO₂ Dyeing

I. Capital Costs

	scCO ₂ Dyeing	Aqueous Dyeing
Equipment cost (HK\$)	8,500k	2,000k
Annual capital charge (HK\$) ^a	1,150k	270K
Labour cost (HK\$/month) ^b	8,000	8,000
Batch time (min)	120	210
Production capacity (kg/batch)	150	300
Production capacity (kg/year) ^c	315k	360k
Capital charge (HK\$/kg)	3.96	1.02

^aThe annual capital charge is 13.5%; ^b1 operator for each machine; ^c14 hr/day and 25 days/month



Economic Evaluation of scCO₂ Dyeing

II. Operational Costs

Compound/utility	scCO ₂		Aqueous		
	Amount/batch	Price (HK\$)	Amount/batch	Price (HK\$)	
Electricity	60 kWh	78	100 kWh	130	
Water	0 m ³	0	5 m ^{3a}	17.5	
Wastewater treatment	0 m ³	0	5 m ³	12.5	
Steam	90 kg	18	1380 kg	276 ^b	
CO ₂	15 kg	0.9	0 kg	0	
Dyes	3 kg	300	6 kg	600	
Dispersing agent	0 kg	0	6 kg	600	
Other chemicals	0 kg	0	3 kg	150	
Maintenance ^c		12		5	
Operating cost (HK\$/kg)		2.73		5.97	
^a For dyeing, washing and rinsing; ^b For dyeing, washing, rinsing and					

drying; ^cMaintenance is 3% of equipment cost

Economic Evaluation of scCO₂ Dyeing

III. Total Processing Costs

	scCO ₂ Dyeing	Aqueous Dyeing
Capital Costs (HK\$)	3.96	1.02
Operational Costs (HK\$)	2.73	5.97
Processing Costs (HK\$/kg)	6.69	6.99

- As energy and water/wastewater costs differ very much from country to country, a concrete comparison of the water and scCO₂ dyeing process is not possible in great detail.
- The water cost in Netherlands is much higher (2.27 €/m³) and the processing for scCO₂ dyeing is 50% lower comparing water dyeing.



Environmental Considerations

Compound/	scCO ₂		Aqueous		scCO ₂	Aqueous
utility	Amount /batch	Amount /kg	Amount /batch	Amount /kg	CO ₂ -emission /kg	CO ₂ -emission /kg
Electricity	60 kWh	0.4 kWh	100 kWh	0.33 kWh	0.24 kg	0.20 kg
Water	0 m ³	0 m ³	5 m ³	0.017 m ³		
Steam	90 kg	0.6 kg	1380 kg	4.6 kg	0.07 kg	0.54 kg
CO ₂	15 kg	0.1 kg	0 kg	0 kg	0.1 kg	0 kg
Dyes	3 kg	0.02 kg	6 kg	0.02 kg		
Dispersing agent	0 kg	0 kg	6 kg	0.02 kg		
Other chemicals	0 kg	0 kg	3 kg	0.01 kg		

- ✓ ScCO₂ dyeing requires less energy with 95% of the CO₂ is recycled and therefore is associated with about 45% lower CO₂-emission, reduces about 100,000 kg of CO₂-emission for yearly production of 300,000 kg polyester fabric.
- \checkmark ScCO₂ dyeing requires only dyes and therefore can save 60% of chemicals.



Does scCO₂ dyeing have a future in the textile industry?

- Environmental advantages
 - Waterless process \rightarrow no wastewater discharge
 - Reuse of CO₂
 - Requires less chemicals and energy
 - Lower CO₂-emission
- ✓ Fully met all of the quality standards for polyester as in water dyeing
 - High colour yields are obtained
 - High levelness of dyeing, i.e. no colour differences at the inside, middle, and outside of the fabric pack
 - Very good washing, rubbing and sublimation fastness properties





Does scCO₂ dyeing have a future in the textile industry?

- ✗ High investment costs of the plant
 - Partly compensated through the lower processing costs
 - Only companies with deep pockets will be able to make such investments
 - The dye industry is typically a very low-margin industry, the price of the dyeing machines must come down
- ➤ ScCO₂ dyeing process now can only be used for polyester, not cotton
 - Several methods have been developed, however...
 - Requires the use of co-solvents or additional chemicals, like surfactant
 - The results were not satisfactory, such as poor fastness properties or deterioration of the fibre properties
 - Much more research based on new concepts and ideas



1HANK You

