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Pilot-scale electrolyser for the cathodic reduction of oxidised C.I. Sulphur Black 1

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Abstract

A multi-cathode electrolyser was used for the direct cathodic reduction of oxidised, dispersed C.I. Sulphur Black 1. Crude C.I. Sulphur Black 1 at concentrations of 80 g L^{-1} and 131 g L^{-1} could be reduced using a cathodic current density of 5.3 mA cm^{-2}. During reduction at pH 12.2–12.6 the redox potential fell from −270 mV to between −550 mV and −600 mV. As crude C.I. Sulphur Black 1 contains considerable amounts of reductants, the current yield was >100% of theoretical value. Energy consumption for the reduction of 1 kg of crude C.I. Sulphur Black was ~1.1 kW h kg^{-1}. The reduced C.I. Sulphur Black 1 was directly used for laboratory dyeing of cotton yarn. Kubelka–Munk values and CIELab coordinates of dyeings using cathodically or chemically reduced dyestuff showed only small differences, indicating similar dyeing behaviour of the reduced dye, independent of the reduction technique.

Keywords: Sulphur dye; C.I. Sulphur Black 1; Cathodic reduction; Black denim; Multi-cathode electrolyser; Cotton

1. Introduction

A considerable amount of the annual production of more than 80,000 tons of C.I. Sulphur Black 1 (SB1) is used for dyeing of black denim (jeans) [1,2]. These dyeings are made on slasher- or rope-type dyeing machines, where only the warp yarn is dyed before the fabric is weaved. During the synthesis, C.I. Sulphur Black 1 is released as an oxidised water insoluble filter cake, which then has to be reduced by alkaline solutions, mainly of sodium sulphide or glucose [3–6]. Commercial liquid preparations of C.I. Sulphur Black 1 contain the dyestuff in its reduced form, which is soluble in alkali. The same reducing agents may also be used in the dyeing process to stabilise the reduced form of the dyestuff during the dyeing procedure, and to inhibit uncontrolled re-oxidation of the dyestuff by atmospheric oxygen [3,7–9].

A reduction potential of −600 mV is required for optimal dyeing results [8,9], which at present is achieved predominantly by the use of chemical reducing agents. These reagents cannot be regenerated, and hence present dyeing techniques suffer from the disadvantages of significant chemical costs as well as the associated environmental costs of high toxicity and high chemical oxygen demand of the waste water [6].

A promising strategy to replace chemical reducing agents is direct cathodic reduction of the dyestuff [10]. Previous studies to reduce crude filter cake of C.I. Sulphur Black 1 by electrochemical methods have successfully demonstrated the viability of direct cathodic dyestuff reduction and application of the reduced dye in continuous pad-steam dyeing processes [11–13]. For exhaust dyeing operations, where only low concentrations of dye are used in the dyebath, the application of indirect cathodic reduction with use of mediator systems has also been proposed [14].

C.I. Sulphur Black 1 can undergo several reduction/oxidation steps in solution, which is the electrochemical basis to use the dyestuff both as colourant and as a mediator. A reduced

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dyestuff molecule is able to transport a reduction capacity of up to six equivalents from the cathode into the dyebath and thus can also act as a redox mediator [8].

The concentration of dye in baths is dictated by the colour depth to be achieved in dyeing. As the current density is limited in exhaust baths of low dyestuff concentrations, there is a need for flexible cells capable of operation at low current densities. In multi-cathode electrolysers a number of cathodes, which operate at low current density, are combined with a common anode. Thus a high overall cell current can be achieved even when the applied cathodic current density remains low [15].

In this paper we describe the use of a pilot-scale multi-cathode electrolyser to prepare 12 L volume of dyebath for black denim dyeing. Reduced C.I. Sulphur Black 1 was prepared by direct cathodic reduction of dispersed oxidised C.I. Sulphur Black 1. The catholyte then was used for dyeing experiments. Black denim dyeing was simulated on a Miniloop laboratory dyeing unit which simulates the slasher-type denim process. Colour depth was analysed as a function of the reduction state, bath temperature and dip time. For comparisons, standard dyeings with use of glucose/dithionite as reducing agent were prepared.

2. Experimental details

2.1. Chemicals

Crude filter cake C.I. Sulphur Black 1 (water containing solid, dye content 50% by mass, DyStar Frankfurt a. M., Germany) was used as delivered. The concentrations cited for the dyestuff are of the crude product.

Primasol® NF (BASF AG, Ludwigshafen a. R., Germany) was used as a wetting agent.

Analytical grade $K_3[Fe(CN_6)]$ and NaOH were used for the determination of reducing equivalents in the catholyte.

For the reference dyeings technical grade glucose (*Reductor D*, Clariant, Basel, Switzerland), sodium dithionite and NaOH were used. Technical grade NaOH was used for the preparation of ground electrolyte.

2.2. Laboratory scale multi-cathode electrolyser

A multi-cathode flow-through electrolyser with three-dimensional cathodes was used for the reduction experiments. The cathode stack was built up of 10 isolated cathode units which were connected to independently adjustable power supply units. All cathode units were connected to the common anode. Anolyte and catholyte were separated by a cation exchange membrane (Thomapor MC-3470). The catholyte flow was parallel to current flow through the porous cathode stack.

The redox potential in the catholyte was measured with a Pt electrode vs. an Ag/AgCl, 3 M KCl reference (potentiometer Metrohm 654 pH-meter, Herisau, Switzerland). A general scheme of the electrolyser is given in Fig. 1.

2.3. Determination of current yield

Current yield was calculated from analytical determination of reducing equivalents formed in solution as a function of electrolysis. Catholyte of 1.25 ml was added to a warm mixture of 30 ml distilled water and 6 ml 1 M NaOH maintained at 50–60 °C. Redox titration with 0.1 M $K_3[Fe(CN)_6]$ was performed under an inert gas atmosphere at 50–60 °C. Potentiometric titration was performed using a titroprocessor equipped with a Pt redox electrode and an Ag/AgCl, 3 M KCl reference (Orion 960 autochemistry system, Boston, MA).

The experiments were structured in two parts:

- phasewise electrochemical reduction of SB1 (phases I–VI) and

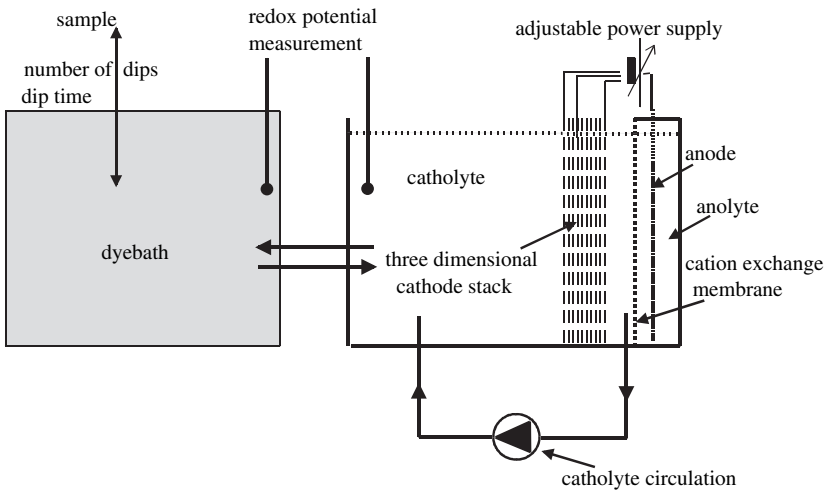


Fig. 1. Scheme of the multi-cathode electrolyser. It consists of three-dimensional cathode stack 20 × 20 cm^2, 10 stainless steel cathodes each 0.19 m^2 area, total area of cathode stack 1.9 m^2, catholyte volume 12 L, circulation 20 L min^{-1}, Pt-mixed oxide coated titan anode 400 cm^2, anolyte 1.9–2 L 1 M NaOH, cathodic current density 0.5–5 A m^{-2}, cell current 1–10 A.

- dyeing experiments following the electrolysis phases II–VI.

During the first phase of the experiment the alkali-soluble leuco form of the dye was produced by cathodic reduction of dispersed SB1. A volume of 12 L of catholyte was prepared. Electrochemical reduction was started with 0.1 M NaOH and 2 ml L^{-1} wetting agent (Primasol® NF) as ground electrolyte. An amount of 963 g oxidised SB1 was dispersed in the catholyte, resulting in a concentration of 80.3 g L^{-1} SB1. The composition of the catholyte and relevant electrochemical data are given in Table 1.

The electrolysis phases II–VI were followed by dyeing experiments. After dyeing, the solutions were pumped back into the electrolyser and cathodic reduction was continued. The dyeing experiments are presented in Section 3. In Table 1, references are made to those data tables which show dyeing results.

2.4. Dyeing procedure

Raw cotton yarn with a titer of 84 tex (mass of 84 g per 1000 m of yarn) was used for the dyeing experiments.

The dyeing procedure simulated a continuous warp dyeing process commonly used for black denim. A laboratory dyeing unit (Mini loop Universal laboratory dyeing machine, Looptex, Lugano, Switzerland) was coupled to the electrolyser. A volume of 4 L of catholyte was pumped into the dyeing vessel.

The procedure included pre-wetting, dips into dyebath, squeezing, air passage and rinsing of the samples (Table 2).

Temperature of dyebath was adjusted to the chosen value and redox potential was measured by means of a Pt redox electrode (potentiometer Metrohm 654 pH-meter, Herisau, Switzerland, Ag/AgCl, 3 M KCl reference electrode). The yarn was pre-wetted in a solution of 3 g L^{-1} wetting agent (Primasol® NF) at room temperature.

After dyeing, the samples were rinsed with soft water at room temperature.

CIELab values of the dyeings were measured with a tristimulus colorimeter (Minolta Chroma-Meter CR 200, geometry d/0°, sample diameter 10 mm, illuminant D65).

Colour fixation on the dyed fabric was determined by *K*/*S* values which were calculated from the diffuse reflectance at 620 nm (Pye Unicam SP 8-100 double beam spectrophotometer, diffuse reflectance sphere 0°/d).

The colour differences ΔE calculated for the respective reference dyeings are given in Tables 4 and 6. The wet rub-fastness of dyeings was determined with the crockmeter according to the standard method [16].

2.5. Reference dyeings

Reference dyeings were performed using dithionite and glucose as reducing agents, using the recipes shown in Table 3.

The dyebath was prepared by addition of the required dye, auxiliaries, NaOH solution and reducing agent. Reference dyeings were performed after dye reduction at 80 °C, at dyestuff concentrations of 80 g L^{-1} and 120 g L^{-1}, with the same dyeing program as used with the electrochemically reduced baths (Table 2). All reference dyeings were carried out above 80 °C, as glucose is suitable as reducing agent only above that temperature.

3. Results and discussion

3.1. Cathodic reduction of SB1

In Fig. 2 is shown the cell voltage as a function of cathode position relative to anode, measured during phases I and V at 10 A and electrolysis times of 230 and 1300 min, respectively.

As typical for multi-cathode electrolysers the cell voltage rises with distance to the anode: from U_1 to U_{10}. In Table 1

Table 1
Experimental conditions of cathodic SB1 reduction during phases I–VI

Phase		NaOH (mol L^{-1})	SB1 (g L^{-1})	Temp. (°C)	Potent. (mV)	*I* (A)	*Q* (A h)	Σ*Q* (A h)	Q_{spez} (A h kg^{-1})	Theor. red. equiv. (mol L^{-1})	Analyt. red. equiv. (mol L^{-1})	U_1 (V)	U_{10} (V)	ΔU (V)
I	Begin	0.10	80.3	21	−270	10	0			0	<0.04	15.4	19.5	4.1
	End	0.31	80.3	40	−549	10	75	75	77.9	0.233	0.644	6.9	8.6	1.7
II (Table 4)	Begin	0.31	80.3	37	−506	0.4/10					0.600	7.8	9.5	1.7
	End	0.41	80.3	40	−588	10	38	113	117.3	0.073	0.900	11.9	13.4	1.5
III (Table 4)	Begin	0.41	80.3	22	−546	1.5/5					0.80	–	–	–
	End	0.43	80.3	46	−541	5	5.1	118.1	122.6	0.016	0.78	–	–	–
IV (Table 4)	Begin	0.43	80.3	20	−516	10						9.1	10.8	1.7
	End	0.53	80.3	38	−603	10	30	148.1	158.8	0.204	0.808	6.4	7.8	1.4
V (Table 6)	Begin	0.53	131.3	40	−534	10						6.9	7.9	1.0
	End	0.73	131.3	31	−578	10	59	207.1	135.9	0.2	1.258	6.7	7.8	1.1
VI (Table 6)	Begin	0.73	131.3	41	−556	10						9.8	10.8	1.0
	End	0.85	131.3	34	−616	10	36	243.1	159.5	0.12	1.304	7.6	8.7	1.1

Calculated concentration of NaOH, concentration of SB1, catholyte temperature, redox potential in catholyte, cell current *I*, charge flow *Q*, cumulative charge flow Σ*Q*, charge per kg of SB1 Q_{spez}, calculated theoretical and analytically determined reducing equivalents in catholyte, cell voltages of cathode 1 U_1, cathode 10 U_{10} and difference in cell voltage between cathodes 1 and 10 $\Delta U = U_{10} - U_1$. Tables for dyeing results are indicated.

Table 2
Dyeing program for black denim

Step no.	Function	Duration of program step (s)
1	Wetting	10
2	Squeezing	10
3	Dip time	11/15/20
4	Squeezing	10
5	Air passage (oxidation)	130
6	Rinse (room temperature)	130
7	Squeezing	20
8	Drying	20
9	Removal of sample and air drying	–

the difference in cell voltage $\Delta U = U_1 - U_{10}$ is shown. Generally ion transport from the anolyte into the catholyte increases conductivity in the catholyte with increasing time of electrolysis, and thus a decrease in ΔU with electrolysis time is observed, e.g. from 4.1 V (phase I) to 1.1 V (phase V). Any increase in $\Delta U = U_1 - U_{10}$ is an indicator for hindered current flow through the three-dimensional electrode stack, for example, due to deposition of oxidised dyestuff in the cathodes [15].

During electrolysis Na^+ ions pass the cation exchange membrane from the anolyte to the catholyte. NaOH concentration in the anolyte was held at a concentration of 1 M NaOH by addition of 50% NaOH. In the catholyte, these Na^+ ions either serve as counter ions of cathodically reduced SB1 or form NaOH from water electrolysis. NaOH concentration given in Table 1 has been calculated on the assumption that all Na^+ ions in the catholyte form NaOH, however, a considerable part of Na^+ ions in the catholyte serves as counter ions for the reduced SB1 (Scheme 1).

From the literature data [8] an average formula mass for the repetitive structure in SB1 can be estimated at 301.2 g mol^{-1}. For full reduction this structural element will require six electrons and equivalent mass is 50.2 g mol^{-1}. Three of six reducible groups will neutralise NaOH in their reduced state and form thiolate or phenolate groups (Scheme 1).

Based on these assumptions a mass of 80.3 g L^{-1} crude SB1 in fully reduced state will neutralise 0.399 mol L^{-1} NaOH and a concentration of 131.3 g L^{-1} crude SB1 will neutralise 0.654 mol L^{-1} NaOH.

As a considerable part of the Na^+ ions in the catholyte are present as counter ions in the reduced SB1 rather small changes in pH were observed during electrolysis. The pH increased from an initial value of 12.2 in phase I to a value of 12.6 in phase VI.

In the initial period of the electrolysis (phase I) an unexpected decrease in redox potential was observed. Immediately

Table 3
Composition of dyebath for reference dyeings

	Recipe 1	Recipe 2
Crude C.I. Sulphur Black 1 (SB1, g L^{-1})	80	120
Glucose (Reductor D, g L^{-1})	60	90
Sodium dithionite (g L^{-1})	12	18
NaOH (50% o.w., mol L^{-1})	0.94	1.41
Wetting agent (Primasol® NF, ml L^{-1})	5	5

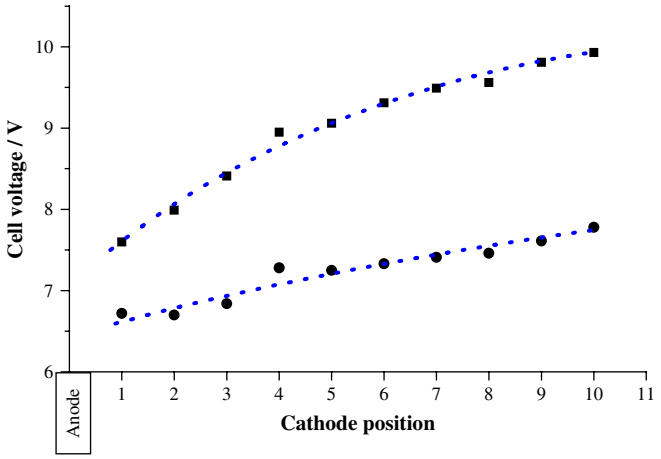
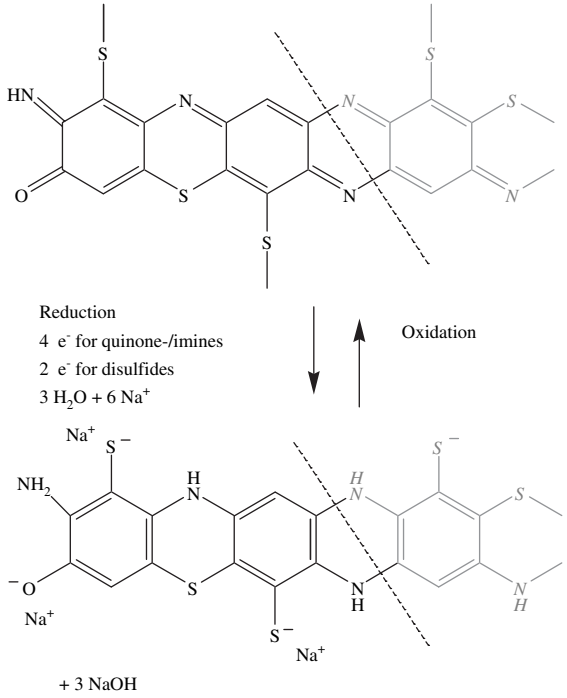


Fig. 2. Cell voltage as a function of electrode position for 10 A cell current. Catholyte at start 0.1 M NaOH, 2 ml L^{-1} wetting agent (Primasol® NF), 963 g oxidised SB1; (■) phase I, 230 min electrolysis time, redox potential −473 mV, temp. 41 °C, (●) phase V, 1300 min electrolysis time, redox potential −573 mV, temp. 31 °C.

after the start of the electrolysis the redox potential in catholyte changed from −270 mV to −600 mV; and at the same time, an intensive evolution of hydrogen was observed. After some minutes the redox potential stabilised near −400 mV and afterwards slowly decreased towards more negative values. A representative curve is shown in Fig. 3.

Initially, the cell current of 10 A, which corresponds to a cathodic current density of 5.3 mA cm^{-2}, exceeds the maximum current density for direct dyestuff reduction. Only a low amount of dispersed dyestuff is reduced on the surface of the cathodes and the major part of the current is spent for



Scheme 1. Reaction model for cathodic reduction of SB1.

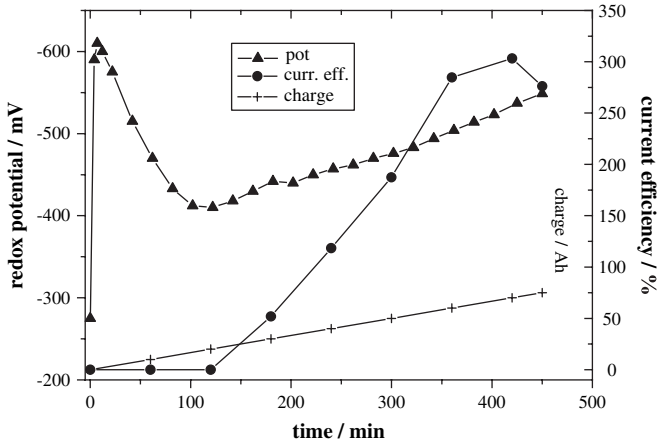


Fig. 3. Redox potential (▲) in catholyte, (●) current efficiency and (+) charge flow as a function of electrolysis time during phase I of reduction experiment.

water electrolysis. The redox potential measured in the catholyte is identified as mixed potential between soluble products formed by direct cathodic reduction of dispersed dyestuff and gaseous hydrogen present in the catholyte.

After higher concentrations of reduced dyestuff have been formed, the redox potential corresponds to the leuco potential of the reduced SB1. The concentration of dissolved reducible dyestuff molecules becomes sufficient to transport the applied cathodic current density and liberation of hydrogen ends.

3.2. Current efficiency

The build up of the reducing equivalents can be monitored by redox titration. Fig. 4 shows titration curves of the catholyte recorded during electrolysis phase I (Fig. 3 and Table 1).

From these data the current efficiency of the reduction can be determined. During the initial phase I (0–120 min) low current efficiency is observed, however, unexpectedly high values of 120–300% were found during the reduction period of 200–400 min.

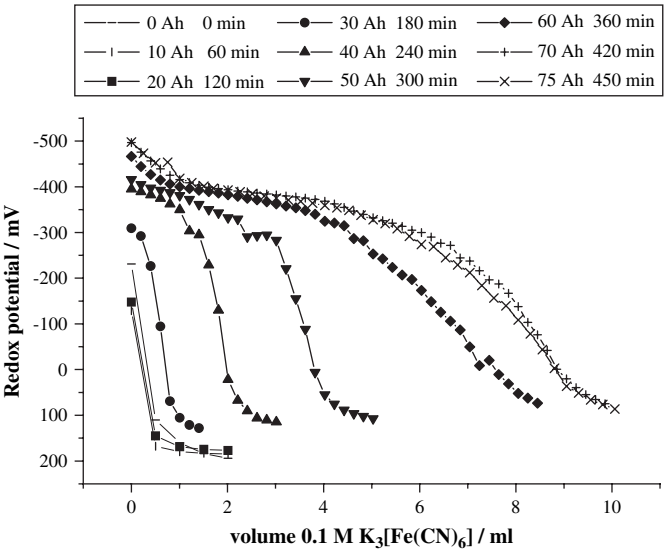


Fig. 4. Titration curves obtained by redox titration of 1.25 ml catholyte with 0.1 M $K_3[Fe(CN)_4]$ (phase I) as a function of charge flow.

SB1 is synthesised by heating aromatic nitro-compounds with sulphur compounds, e.g. sodium sulphide. Thus the structure of the dyestuff is not well defined and various structures have been proposed in the literature [1,2,8]. During the synthesis of SB1 the crude dyestuff has been oxidised by air oxygen, precipitated, filtered and rinsed. Dependent on the technical conditions this crude ''oxidised'' dyestuff contains considerable amounts of reducing equivalents inside the particles. These reducing equivalents are released during cathodic reduction and dissolution of SB1 and here add to the equivalents introduced electrochemically. Determination of the reducing equivalents in the catholyte by redox titration with $K_3[Fe(CN)_6]$ thus exhibits an apparent current yield of greater than 100%. This effect is particularly observed after a charge flow of 40–70 A h (Figs. 3 and 4).

Complete electrochemical reduction of the dyestuff is achieved, when all possible sites in the SB1 molecule are present in reduced state. At a concentration of 80.3 g L^{-1} SB1 a concentration of 0.80 mol L^{-1} reducing equivalents are estimated for full reduction and at a concentration of 131.2 g L^{-1} full reduction of SB1 corresponds to 1.31 mol L^{-1} reducing equivalents present in the solution [8]. The titration results given in Table 1 indicate that complete dyestuff reduction had been achieved at the end of electrolysis phases (II–VI).

3.3. Energy consumption

Based on an average cell voltage U and the charge flow given in Table 1 an estimation of energy consumption P for reduction of 1 kg crude SB1 is possible (Eq. (1)).

$$P = U \times Q_{spez} \times 0.001 \quad (1)$$

Where P is the energy consumption for reduction of 1 kg SB1 in kW h kg^{-1}, U the average cell voltage of cathode stack in V, and Q_{spez} the charge per kg of SB1 in A h kg^{-1}.

A charge flow of 113 A h was required to reduce 963.6 g SB1 in 12 L catholyte to a potential of −588 mV (end of phase II). Based on an average cell voltage $U = 9$ V, a value of $P = 1.06$ kW h kg^{-1} is obtained. Total charge flow up to end of phase V reached 207.1 A h required to reduce 1444 g SB1. Based on an average cell voltage of 8 V the energy consumption to reduce 1 kg of SB1 then will be 1.08 kW h kg^{-1}.

3.4. Dyeing experiments

The solution of cathodically prepared SB1 was used directly for dyeing experiments. About 4 L of catholyte was pumped into the laboratory dyeing unit, the dyebath was heated to dyeing temperature and redox potential was measured. At the end of a dyeing series the dyebath was pumped back to the electrolyser and cathodic reduction was continued. Relevant conditions and results of the dyeings are shown in Tables 4 and 6. Dyeings were made with a dyestuff concentration of 80 g L^{-1} and 131.3 g L^{-1} SB1.

Table 4
Dyeing experiments (phases II–IV)

Phase/sample	Red. equiv. temp. (mol L^{-1}/°C)	Redox potential (mV)	Dip (s)	CIELab			ΔE	K/S	$\Delta K/S$
				L^*	a^*	b^*			
Phase II	0.90 mol L^{-1}								
1	30	−502	11	30.58	−1.68	−4.68		7.16	
2	50	−491	11	25.54	−1.40	−4.24		10.51	
3	83	−567	11	22.18	−0.69	−3.07	5.62	13.30	−6.34
Phase III	0.78 mol L^{-1}								
4	44	−536	11	24.52	−0.95	−3.48		12.90	
5	84	−544	11	18.41	−0.26	−2.12	1.72	15.96	−3.68
6	27	−546	15	25.51	−1.52	−3.87		10.93	
7	57	−538	15	22.35	−0.85	−3.39		12.00	
8	83	−536	15	18.54	−0.18	−2.29	1.99	19.62	1.12
9	47	−541	20	20.80	−0.72	−3.34		12.53	
10	92	−542	20	16.23	+0.03	−1.67	0.72	23.40	4.22
Phase IV	0.81 mol L^{-1}								
11	33	−605	15	19.34	−0.65	−2.68		17.88	
12	50	−605	15	19.45	−0.20	−2.36		17.88	
13	86	−597	15	14.49	+0.32	−1.37	2.21	22.82	4.32
14	85	−590	20	16.07	+0.17	−1.63	0.63	21.23	2.05

Crude Sulphur Black 1 of 80 g L^{-1}, redox equivalents in dyebath/dyebath temperature, redox potential, dip time, CIELab coordinates, K/S (620 nm), and colour differences ΔE and $\Delta K/S$ calculated reference dyeing in Table 5.

A concentration of 0.6 mol L^{-1} reducing equivalents was obtained in the dyebath for samples 1–3 (Table 4). During phase III (samples 4–10) low cell current was used to compensate only for the oxidative load brought into the bath during the dyeing experiment. The titration data thus even indicate a slight decrease in concentration of reducing equivalents in the bath from 0.80 mol L^{-1} to 0.78 mol L^{-1} (Table 1).

During phase IV the catholyte was reduced by charge flow of 30 A h, the redox potential in the catholyte decreased from −516 mV to −603 mV. Then the dyeing experiments 11–14 were performed (Table 4).

The high concentration of reduced dyestuff in the bath stabilised the redox potential in the dyebath. In the dyeing experiments that followed phases III–VI, the redox potential varied less than ±10 mV.

In reference dyeing experiments a more negative redox potential of −640 mV to −700 mV was observed. However, the interpretation of a redox potential measured in alkaline glucose solutions is difficult [9]. Reducing power of glucose bases on complex reactions and strongly depends on temperature in bath and alkalinity. Thus the redox potential of the reference dyebaths depends on a number of experimental factors, which include the concentration of sulphur dye and rate of oxygen uptake on the surface of the dyebath.

The increase in colour fixation with dyebath temperature can be seen both at the CIELab coordinates and the K/S function. Colour fixation in terms of K/S value almost doubles with increase of temperature from 30 °C to 83 °C. This result can be explained with kinetically limited dyestuff adsorption on the substrate, which accelerates at higher temperature. Increasing dyebath temperature thus increases the rate of dyestuff diffusion and exhaustion. In technical black denim dyeing operations, a dyebath temperature of about 85–90 °C is recommended.

The dependence of dyestuff uptake on dyeing temperature is shown in Fig. 5. At high dyestuff concentration of 131 g L^{-1} SB1 saturation limits the increase in colour depth. Thus L^* values are not directly related to the increase in dyestuff concentration from 80 g L^{-1} to 131 g L^{-1}. However, the behaviour of electrochemically reduced dyestuff and conventional reduced dyestuff is found to be similar under the applied experimental conditions.

The influence of dip time can be seen in the colour strength (K/S) and CIELab coordinates. At given range of temperature longer immersion in the dyebath increased K/S and decreased the lightness of the dyeings. As dyeing equilibrium is not established during the short dip time, the longer time of immersion increased dye exhaustion (expts. 4/7/9; expts. 5/8/10).

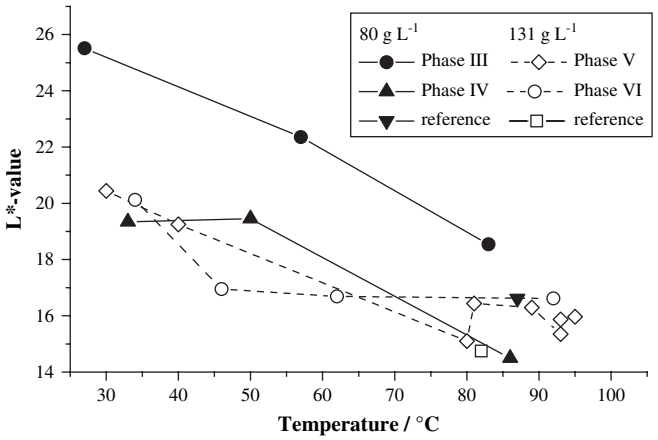


Fig. 5. L^* value as a function of dyeing temperature, (◆) experiments 6–8, (▲) experiments 11–13, (▼) reference dyeings 80 g L^{-1}, (◇) experiments 18–25, (○) experiments 26–29, (□) reference dyeing 120 g L^{-1}, for electrochemically reduced dyebaths and standard dyeings.

Table 5
Reference dyeings

Sample no.	Temperature (°C)	Redox potential (mV)	Dip (s)	CIELab			*K/S*
				*L**	*a**	*b**	
15	86 ± 3	−656 ± 3	11	16.71 ± 1.55	−0.15 ± 0.20	−1.89 ± 0.23	19.64 ± 1.52
16	87 ± 2	−685 ± 16	15	16.61 ± 0.40	−0.12 ± 0.08	−1.78 ± 0.13	18.50 ± 0.57
17	88 ± 2	−643 ± 5	20	15.56 ± 0.45	−0.01 ± 0.15	−1.41 ± 0.05	19.18 ± 1.04

Average values of three dyeing experiments; 80 g L^{-1} crude C.I. Sulphur Black 1, temperature, redox potential, dip time, CIELab coordinates, *K/S* (620 nm).

In experiment 14, although the dip time was extended from 15 s to 20 s, the increase in colour depth was not substantial due to saturation which nearly had been reached at a dip time of 15 s.

In Table 5 reference samples are presented. From the chemical nature of SB1 it can be assumed that the reducing method used will also influence the composition and structure of reduced dyestuff species formed in the dyebath, and it is known that both the type of reducing agent and oxidation method influence the final shade in dyeings.

The CIELab coordinates and *K/S* values of the reference dyeings obtained using conventional reducing agents (glucose/dithionite) are shown for 80 g L^{-1} SB1 in Table 5 and for a dye concentration of 120 g L^{-1} in Table 7. In Table 4 colour difference of samples 3, 5, 8, 10, 13 and 14 to comparable reference experiments in Table 5 is presented.

When the CIELab coordinates of the electrochemically reduced and the reference dyeings at similar temperature are compared, rather small differences are observed, which indicate comparable dyeing behaviour of cathodically reduced SB1. The colour difference (ΔE) between samples 5, 8, 10, 13 and 14 and the reference dyeings ranged from 0.63 to 2.2, and $\Delta K/S$ varied from −6.34 (expt. 3) to +4.32 (expt. 13); a positive difference in $\Delta K/S$ indicates lighter reference dyeings. Darker dyeings were obtained for an immersion time of 15–20 s, however, the strong influence of dyebath temperature prevents a detailed analysis of the small differences in colour depth. Even rather small variations in dyebath temperature will influence the final colour depth considerably.

Before reduction phase V crude SB1 was added to increase the SB1 concentration to 131.3 g L^{-1}. Results of dyeings are shown in Table 6. In phase V the dyebath was reduced with a charge flow of 59 A h. The concentration of the reducing equivalents in the catholyte increased from 0.808 mol L^{-1} to 1.258 mol L^{-1}. Theoretically a charge flow of 59 A h would introduce a concentration of 0.2 mol L^{-1} reducing equivalents in the catholyte. Again experimental current efficiency exceeded 100%.

Reference dyeings for a concentration of 120 g L^{-1} SB1 are shown in Table 7, which indicate a limited increase in colour depth as compared to the results obtained with 80 g L^{-1} SB1. This can be explained with both, saturation effects due to limited dyestuff uptake by the cotton yarn and limited sensitivity of CIELab and *K/S* measurements on black dyeings. Anyhow colour differences as ΔE or $\Delta K/S$ between standard dyeings and electrochemical dyeings are low.

In Table 6 colour differences ΔE and $\Delta K/S$ for the dyeings 20–25 and 29 are shown. For comparison of results in Tables 6 and 7 it should be considered that electrochemical dyeings were performed at a concentration of 131 g L^{-1} crude SB1, while the reference dyeings were performed at lower

Table 6
Dyeing experiments (phases V and VI)

Phase/sample	Temperature (mol L^{-1}/°C)	Redox potential (mV)	Dip (s)	CIELab			ΔE	*K/S*	$\Delta K/S$
				*L**	*a**	*b**			
Phase V	1.26 mol L^{-1}								
18	30	−578	15	20.44	−0.68	−3.06		14.16	
19	40	−575	15	19.25	−0.39	−2.73		23.40	
20	80	−566	15	15.10	+0.32	−1.03	0.58	24.01	3.84
21	81	−565	15	16.44	+0.25	−1.51	1.69	24.01	3.84
22	89	−567	15	16.29	+0.55	−0.81	1.71	22.26	2.09
23	93	−570	15	15.35	+0.55	−0.76	0.99	20.29	0.12
24	93	−566	15	15.87	+0.59	−0.35	1.63	23.40	3.23
25	95	−563	15	15.97	+0.84	−0.35	1.77	30.26	10.09
Phase VI	1.30 mol L^{-1}								
26	34	−616	15	20.12	−0.32	−2.57		19.42	
27	46	−610	15	16.95	+0.20	−1.79		18.62	
28	62	−609	15	16.69	+0.47	−1.12		22.82	
29	92	−607	15	16.62	+0.94	−0.28	2.33	26.04	5.87

Crude C.I. Sulphur Black 1 of 131.3 g L^{-1}, redox equivalents in dyebath/dyebath temperature, redox potential, CIELab coordinates, *K/S* (620 nm) and colour differences ΔE and $\Delta K/S$ calculated to corresponding reference dyeing in Table 7.

Table 7
Standard dyeings

Sample no.	Temperature (°C)	Redox potential (mV)	Dip (s)	CIELab			*K/S*
				*L**	*a**	*b**	
30	81 ± 1	−708 ± 6	10	16.48 ± 0.25	−0.10 ± 0.08	−2.02 ± 0.13	20.29 ± 0.46
31	82 ± 1	−730 ± 12	15	14.75 ± 0.25	+0.23 ± 0.10	−1.48 ± 0.06	20.17 ± 1.00
32	82 ± 3	−693 ± 9	20	15.03 ± 0.04	+0.14 ± 0.07	−1.37 ± 0.07	21.70 ± 2.12

Average values of three dyeing experiments; 120 g L^{-1} crude C.I. Sulphur Black 1, temperature, redox potential, CIELab coordinates, *K/S* (620 nm).

concentration of 120 g L^{-1} crude SB1. Thus the higher *K/S* values in the case of cathodic dyestuff reduction are also due to the approximately 10% higher dyestuff concentration.

Values for wet rub-fastness of dyeings 3, 5, 8, 10, 13 and 14 which were dyed with 80 g L^{-1} crude SB1 at dyebath temperature 83–92 °C were determined as 1.0 (13 determinations). Comparable reference dyeings 15–17 showed average values for wet rub-fastness of 1.1 (seven determinations). Due to the dyeing procedure used rub-fastness in general is low, however, there is some indication that the considerable surplus of reducing agents present in the reference dyebaths could slightly improve rub-fastness.

4. Conclusions

Direct cathodic reduction of oxidised crude C.I. sulphur Black 1 to its corresponding leuco form could be achieved at concentrations of 80 g L^{-1} and 131 g L^{-1} by means of a multi-cathode electrolyser. After an initial phase of hydrogen formation, 10 A cell current with 5.3 mA cm^{-2} current density could be applied without bipolar behaviour of the multi-cathode electrolyser. Analytically determined current yield reached values above 100% of theoretical, due to the presence of reduced components inside the SB1 filter cake.

Dyeings obtained with electrochemically reduced SB1 are similar to reference dyeings with glucose/dithionite as reducing agents. When complete dye reduction has been achieved, colour depth is mainly influenced by variation of composition of dyebath, dyebath temperature and dip time.

In general electrochemical dyeings tend to result in higher colour yield for a given dyestuff concentration, compared to standard dyeings. However, this assumption has to be proven by more detailed experimental analysis.

Energy consumption for cathodic reduction of crude C.I. Sulphur Black 1 into the leuco form could be estimated as 1.1 kW h kg^{-1}.

The experiments demonstrate the potential of direct electrochemical reduction to replace conventional reducing agents used at present.

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