Novel leuco sulfur dye compositions obtainable at current densities between 50 mA/cm² and 500 mA/cm² and a flow velocity in the range from 0.1 m/s to 2 m/s and preferably in the range from 0.1 to 0.4 m/s, their production and their use for dyeing cellulosic material.
Fig. 1: Production Sample 1 (j = 100mA/cm²)
Fig. 2: Production Sample 2 (j = 20mA/cm²)
Fig. 3: Production Sample 3 ($j = 0.48 \, \text{mA/cm}^2$)
Fig. 4: Production Sample 4
Fig. 5: C.I. Sulfur Black 1 (sulfidically reduced)
Fig. 6: Production Sample 5 (j = 100 mA/cm²)
Fig. 7: Production Sample 6 (j = 10 mA/cm²)
Fig. 8: C.I. Vat Blue 43 (sulfide-reduced)
NOVEL QUINONEIMINE SULFUR DYE COMPOSITIONS, PRODUCTION THEREOF AND USE FOR DYEING CELLULOSIC MATERIAL

[0001] The present invention relates to novel leuco sulfur dye compositions of the quinoneimine sulfur dye group and also to their production by electrochemical reduction through controlled variation of the electrochemical processing conditions employed.

[0002] Quinoneimine sulfur dyes comprise that group of dyes which are formed for example by reaction of polyamidated phenols, halobenzenes, indophenols or indoanlines with sulfur, alkali metal sulfides or alkali metal polysulfides in aqueous or alcoholic media. Violet, blue, green, reddish brown and black sulfur dyes in particular comprise this group of dyes. The resulting oligomeric or polymeric products contain organic structural repeat elements (for example phenothiazine, thiazine, thianthrene and phenoxazine substructures) which are joined together via disulfide bridges. The reference Angewandte Chemie 60 (1948), 141-147 describes these structures.

[0003] To dye with these sulfur dyes, they are converted by various methods of reduction into a ready-to-dye leuco form which, on the one hand, reduce the quinoneimine functionalities and, on the other, reductively cleave the disulfide bridges. The resulting leuco compounds generally have lower molar masses and comprise a wide molecular range of species. They are soluble in an aqueous alkaline medium and can be used for dyeing cellulose material.

[0004] In the presence of suitable oxidizing agents, examples being oxygen in the air, peroxides or bromate, the dye is more or less completely oxidized back in accordance with the hereinbelow indicated equation, where R represents organic repeat structural elements, for example phenothiazine, thiazine, thianthrene or phenoxazine substructures.

\[
\begin{align*}
R - S - S - R & \xrightarrow{\text{reduction}} R - S' + R - S' \\
R - S' + R - S' & \xrightarrow{\text{oxidation}} R - S - S - R
\end{align*}
\]

[0005] As well as fully oxidized sulfur dyes, which are only converted into the ready-to-dye leuco forms in the course of the actual dyeing operation, by addition of organic or inorganic reducing agents, more or less ready-to-dye prereduced leuco sulfur dye brands are also available on the market, an example being Casulon® Carbon CMR. These are preferably produced on a large industrial scale by addition of inorganic or organic reducing agents, for example sodium hydrogen sulfite or glucose in an alkaline medium.

[0006] These existing processes have the disadvantage that very high concentrations of waste products and salt burdens due to the reducing agents used are present and lead to high COD and TOC burdens in the dyehouse wastewater. These by-products can only be removed, upstream of the wastewater treatment stage, with considerable engineering commitment and through costly and inconvenient measures, for example membrane techniques.

[0007] An alternative, environmentally friendly reduction method is known from the examples which are given in the documents D È 1906083 and EP 10122120. DE 1906083 recommends dye reduction by cathodic reduction in aqueous solution at current densities between 5 mA/cm² and 50 mA/cm². However, this process is not utilisable in the case of commercially available prereduced sulfur dyes, which are typically admixed with further stabilising reducing agents in the dyeing solution, owing to severe evolution of hydrogen during the reduction. The EP 10122120 patent specification describes a process for reducing sulfur dyes at a current density in the range from 0.5 mA/cm² to 5 mA/cm².

[0008] It has now been found that, surprisingly, utilizing current densities between 50 mA/cm² and 500 mA/cm² coupled with a flow velocity in the range from 0.1 m/s to 0.4 m/s makes available novel leuco sulfur dye compositions which are not preparable by conventional reduction using organic or inorganic reducing agents.

[0009] This invention accordingly provides novel leuco sulfur dye compositions obtainable at current densities between 50 mA/cm² and 500 mA/cm² and preferably between 50 mA/cm² and 150 mA/cm² and a flow velocity in the range from 0.1 m/s to 2 m/s and preferably in the range from 0.1 to 0.4 m/s.

[0010] The process for producing the present invention’s leuco sulfur dye compositions is novel and likewise forms part of the subject matter of this invention. To avoid hydrogen evolution at these high current densities, the electrochemical reduction is carried out in the presence of fairly high dye concentrations by starting at a concentration of 80 g/l and an initial current density of 0.5 mA/cm² and continuously increasing the concentration to 500 g/l and the current density to 500 mA/cm². The process of the present invention makes it possible to reduce dye concentrations down to 500 g/l.

[0011] The present invention’s leuco sulfur dye compositions are produced in an alkaline medium, preferably at a pH >9.5. It is preferable to employ alkaline solutions of alkali metal salts, especially sodium hydroxide, potassium hydroxide or sodium carbonate as conducting electrolyte. It is particularly preferable to utilize dilute aqueous sodium hydroxide solution. The concentration of added conducting salt is between 0.1 mol/l to 5 mol/l preferably between 0.1 mol/l to 1.5 mol/l.

[0012] Alternatively, hydrogen evolution can be prevented by catalytic addition of Bunte salts of the general formula

\[
R - S - \text{SO}_3\text{Na}_x
\]

where R represents organic repeat structure elements, examples being phenothiazine, thiazine, thianthrene or phenoxazine substructures, or by catalytic addition of chemical reducing agents, examples being sodium dithionite, organic sulfonic acids and/or organic sugars. The amounts used can be up to 5% by weight of the starting amount used of the sulfur dye to be reduced. Again, after addition of the Bunte salts or of the reducing agents, starting at 80 g/l and an initial current density of 0.5 mA/cm² the concentration is continuously increased to 500 g/l.

[0013] Essentially all divided flow through cells are suitable for producing the leuco sulfur dye compositions of the present invention. The cathode used can be not only a massive plate electrode but also a three-dimensional cathode.

[0014] The leuco sulfur dye compositions of the present invention are preferably produced at 20 to 135°C, and more preferably at 20 to 95°C.

[0015] If desired, the reduction can also be carried out in the presence of commercially available wetting agents, examples being lignosulfonates.

[0016] The process of the present invention is preferably employed for reducing C.I. Leuco Sulfur Black 1 or C.I. vat
Blue 43. In principle, mixtures of different sulfur dyes can be reduced by the present invention’s process too.

[0017] The concentration of reduction equivalents which is recorded in the case of the present invention’s reduction of C.I. Leuco Sulfur Black 1 is between 150 Ah/kg and 534 Ah/kg based on 1 kg of dry solid dye.

[0018] The concentration of reduction equivalents which is recorded in the case of the present invention’s reduction of C.I. Vat Blue 43 is between 75 Ah/kg and 225 Ah/kg based on 1 kg of dry solid dye.

[0019] The composition of the respective leuco sulfur dye mixtures is determined using common HPLC techniques and materials as described for example in the document DE 10 120 821.

[0020] Table 1 shows the result of the HPLC spectra of sulfidically reduced C.I. Sulfur Black 1, compared with samples 1 to 3, which were electrochemically reduced at different current densities, sample 1 being reduced by the process of the present invention, sample 2 as described in the document DE 1906083 and sample 3 as described in EP 10122210.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dye 1 retention time (area %)</th>
<th>Dye 2 retention time (area %)</th>
<th>Dye 3 retention time (area %)</th>
<th>Dye 4 retention time (area %)</th>
<th>Dye 5 retention time (area %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1 (FIG. 1)</td>
<td>j = 100 mA/cm²</td>
<td>2.8 min</td>
<td>3.0 min</td>
<td>(31.7)</td>
<td>(65.5)</td>
</tr>
<tr>
<td>Sample 2 (FIG. 2)</td>
<td>j = 20 mA/cm²</td>
<td>1.6 min</td>
<td>2.5 min</td>
<td>2.9 min</td>
<td>(81.3)</td>
</tr>
<tr>
<td>Sample 3 (FIG. 3)</td>
<td>j = 0.48 mA/cm²</td>
<td>1.6 min</td>
<td>2.5 min</td>
<td>1.9 min</td>
<td>(1.15)</td>
</tr>
<tr>
<td>Sample 4 (FIG. 4)</td>
<td>j = 1.0 mA/cm²</td>
<td>1.6 min</td>
<td>2.5 min</td>
<td>2.9 min</td>
<td>(43.72)</td>
</tr>
<tr>
<td>C.I. Sulfur Black 1 (sulfide-reduced)</td>
<td>(FIG. 5)</td>
<td>1.6 min</td>
<td>2.0 min</td>
<td>2.5 min</td>
<td>2.9 min</td>
</tr>
</tbody>
</table>

[0021] Surprisingly, the use of high current densities >50 mA/cm² in conjunction with the high flow velocity, which permits an optimal dye transport to the electrode, leads for C.I. Sulfur Black 1 to a narrower distribution of species and thus to a narrower molecular distribution.

[0022] Table 2 shows the result of the HPLC spectra of sulfidically reduced C.I. Vat Blue 43 compared with samples 6 to 8, which were electrochemically reduced at different current densities, sample 6 having been reduced by the process of the present invention and sample 7 as described in the document EP 10122210.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dye 1 retention time (area %)</th>
<th>Dye 2 retention time (area %)</th>
<th>Dye 3 retention time (area %)</th>
<th>Dye 4 retention time (area %)</th>
<th>Dye 5 retention time (area %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 6 (FIG. 6)</td>
<td>j = 100 mA/cm²</td>
<td>4.21 min</td>
<td>6.03 min</td>
<td>6.97 min</td>
<td>9.77 min</td>
</tr>
<tr>
<td>Sample 7 (FIG. 7)</td>
<td>j = 10 mA/cm²</td>
<td>3.02 min</td>
<td>—</td>
<td>7.92 min</td>
<td>10.99 min</td>
</tr>
<tr>
<td>C.I. Vat Blue 43 (sulfide-reduced)</td>
<td>(FIG. 8)</td>
<td>5.15 min</td>
<td>6.10 min</td>
<td>6.45 min</td>
<td>7.10 min</td>
</tr>
</tbody>
</table>

[0023] The leuco sulfur dye solutions of the present invention can be applied to the fiber not only by the classic methods of dyeing, which utilize a large excess of hydrosulfide (Na2S), but also with optimized dyeing recipes under protective gas or electrochemically as described in the Offenlegungsschrift DE 10234825 A1. The reducing conditions merely serve to compensate the atmospheric oxygen introduced into the dyeing liquor. This makes it possible to obtain a wastewater which is low in salt, COD and TOC. The use of the present invention’s leuco sulfur dye compositions accordingly provides a substantial ecological and economic benefit.

[0024] Alternatively, it is also possible for the electrochemical reduction to produce the present invention’s dye compositions also to be produced directly in the dyebath.

[0025] An electrolysis, for example in a cell which is divided by a cation exchange membrane and contains a stainless steel cathode and a stainless steel mixed oxide coated titanium electrode as an anode, is carried out in the presence of conducting electrolyte at current densities in the range from 50 mA/cm² to 500 mA/cm² and preferably between 50 mA/cm² and 150 mA/cm² and that of a flow velocity in the range from 0.1 m/s to 2 m/s and preferably in the range from 0.1 to 0.4 m/s, the dyebath circulating through the material to be dyed and being pumped as a bleed stream through the cathode space, so that the dyebath is continually regenerated through exchange with the catholyte. The catholyte contains the sulfur dye to be reduced, for example C.I. Sulfur Black 1 or C.I. Vat Blue 43, if desired wetting agents, conducting electrolyte, preferably alkaline solutions of alkali metal salts, especially sodium hydroxide, potassium hydroxide or sodium carbonate, more
preferably dilute aqueous sodium hydroxide solution, and also conducting salt. The concentration of conducting salt added is between 0.1 mol/l to 5 mol/l and preferably between 0.1 mol/l to 1.5 mol/l.

[0026] The cellulosic material, ready prepared for dyeing, is in the dyebath.

[0027] The dyeing program consists of a plurality of phases:

[0028] reducing and heating phase

[0029] dyeing and cooling phase

[0030] completion of dyeing by oxidation of sulfur dye, rinsing and drying.

[0031] Coloristic assessment of the dyeings obtained with the leuco sulfur dyes of the present invention shows that, compared with leuco sulfur dyes conventionally produced through use * of chemical reducing agents, they are notable for a distinctly lower fraction of waste products having no affinity for fiber. This leads to greater cleanliness in hue coupled with a simultaneous shift in hue for the electrochemically produced leuco sulfur dye compositions. C.I. Sulfur Black 1 was observed to undergo a distinct shift in hue toward redder, redder cleaner. These effects are observed with mutatis mutandis for the electrochemical reduction of C.I. vat Blue 43.

[0032] The dyeing is assessed calorimetrically by color locus measurement in accordance with DIN 6174 and DIN 5033.

[0033] As the L values in table 3 show, an electrochemical reduction at increased current densities in accordance with the process of the present invention achieves the same color strength for lower amounts of dye.

| TABLE 3 |
|---|---|---|---|
| | L (lightness) | a (red-green) | b (yellow-blue) |
| C.I. Sulfur Black 1 | | | |
| (sulfide-reduced) | 280 g | 16.03 | -0.33 | -1.26 |
| Sample 1 | 247.2 g | 16.01 | -0.38 | -1.67 |
| (j = 100 mA/cm²) | | 15.68 | -0.16 | -1.53 |
| Sample 3 | 283.2 g | | |
| (j = 0.48 mA/cm²) | | | |

[0034] Depth of shade and hue is describable by means of an exhaust dyeing as a function of dye concentration and current density used through color locus measurement of the dyeings (10% sulfide dyeing). In the case of C.I. vat Blue 43 too a distinct shift in hue is obtained as a function of current density used (redder in the case of a higher current density), as shown in table 4.

| TABLE 4 |
|---|---|---|
| | L (lightness) | a (red-green) | b (yellow-blue) |
| C.I. vat Blue 43 | 20.30 | 1.94 | -23.39 |
| (sulfide-reduced) | | | |
| Sample 4 | 30.31 | 1.24 | -22.36 |

[0035] Besides the hue aspects it is remarkable that the sulfur dyes of the present invention for a comparable color strength require up to 10% less sulfur dye paste and thus up to 10% less raw material than the chemically produced leuco sulfur dye solutions.

[0036] The electrochemically reduced leuco quinonimine sulfur dye compositions of the present invention can be stabilized by isolating them as a solid material.

[0037] The present invention accordingly also provides a process for producing the present invention’s reduced quinonimine sulfur dyes in their solid form, by lowering the pH to <9 and/or drying the electrochemically reduced leuco quinonimine sulfur dye solutions.

[0038] One form of the present invention’s isolation as a solid material consists in reducing the pH to ≤9, which can be effected by adding organic acids, mineral acids and carbon dioxide to the reduced solutions. Furthermore, the reduced sulfur dye solutions can be adjusted by addition of water to a pH ≤9 to thereby precipitate the dyes. The products of the present invention are then won by filtration and subsequent drying. In the process, the salts and the organic constituents without fiber affinity remain in solution. The filtrate obtained can be oxidatively treated and the COD burden thus markedly reduced. The dry sulfur dyes thus obtained have a residual salt content <10% by weight based on total mass.

[0039] The second way to isolate solid leuco quinonimine sulfur dye consists in fully drying the as-reduced solution. Drying can be effected using customary drying systems and apparatuses (evaporators for example), for example by spray drying or thin film drying and the dried product can be further comminuted to the desired particle size in order that the dry reduced alkali-soluble product may be converted into the form of pellets, powder or chips for example. Formulations with suitable auxiliaries by mixing are also possible. Freeze drying is another possibility.

[0040] The dry leuco sulfur dyes thus obtained can have a concentration of reduction equivalents between 150 A/h/kg and 534 A/h/kg in the case of C.I. Leuco Sulfur Black 1 and between 75 A/h/kg and 225 A/h/kg in the case of C.I. vat Blue 43, based on 1 kg of dry solid dye.

[0041] A leuco sulfur dye is considered a dry product when its water content is ≤5% by weight and preferably ≤2% by weight based on the entire product.

[0042] The process described provides a very simple way to obtain the leuco sulfur dyes of the present invention in their stabilized (without addition of further sulfides and other auxiliaries) leuco sulfur dye compositions in very high concentration which are virtually free of sulfides and, when isolated by precipitation at comparatively low pH values, are free of salts and organic constituents without fiber affinity. The content still present is ≤1% by weight and preferably
≤0.5% by weight based on the entire product. The dyes produced are notable for stability to atmospheric oxidation.

[0043] The leuco sulfur dye solutions used to isolate the products of the present invention can have concentrations in the range from 20 to 600 g/L for dye used.

[0044] The products of the present invention, once dissolved in water and if appropriate admixed with alkali, can be used for dyeing cellulosic material or leather. The dry leuco sulfur dye compositions of the present invention can, after dissolving, be applied to the fiber not only by the classic methods of dyeing, which operate with an excess of chemical reducing agents, but also using optimized dyeing recipes under protective gas or electrochemically, as described in the Offenlegungschrift DE 10234825 A1. The reductive conditions merely serve to compensate the atmospheric oxygen introduced into the dyeing liquor. The use of the leuco sulfur dye compositions of the present invention therefore constitutes a substantial ecological and economic benefit. The color properties of the products correspond to the color properties of the samples described in the application DE 102004046001.4.

[0045] The examples which follow illustrate the invention.

PRODUCTION EXAMPLE 1 (SAMPLE 1)

[0046] A flowthrough cell divided by a cation exchange membrane (Nafion® 424) is used to electrolyze an aqueous suspension of an as-manufactured C.I. Sulfur Black 1 press-cake. A small amount of dye is used at the beginning, and is gradually increased in the course of the electrolysis. The reaction is started with 156.9 g of C.I. Sulfur Black 1 reckoned dry in 2 L of water comprising 8 mL of 50% aqueous sodium hydrosulfite solution and 4 mL of Primasol NF wetting agent and continued up to an amount of 2271 g of C.I. Sulfur Black 1 reckoned dry in a total volume of 5.815 L. The electrolysis is conducted over 3510 minutes using a current density of 100 mA/cm² coupled with a flow velocity of 0.2 m/s. The level of reducing equivalents which is ascertainable after the electrolysis is 4.2, which corresponds to a charge quantity of 378 Ah per kg of dye. The solution thus produced can be used for dyeing purposes either without further additions or with minimized additions of reducing agents.

[0047] The HPLC spectrum of the reaction product is reproduced in FIG. 1.

PRODUCTION EXAMPLE 2 (SAMPLE 2)

[0048] A flowthrough cell divided by a cation exchange membrane (Nafion® 424) is used to electrolyze a C.I. Sulfur Black 1 suspension at a current density of 20 mA/cm² as described in DE 1906083.

[0049] The HPLC spectrum of the reaction product is reproduced in FIG. 2.

PRODUCTION EXAMPLE 3 (SAMPLE 3)

[0050] A flowthrough divided by a cation exchange membrane (Nafion 424) is used to electrolyze a C.I. Sulfur Black 1 suspension at a current density of 0.48 mA/cm² as described in EP 10122210.

[0051] The HPLC spectrum of the reaction product is reproduced in FIG. 3.

PRODUCTION EXAMPLE 4 (SAMPLE 4)

[0052] A flowthrough cell divided by a cation exchange membrane (Nafion® 424) is used to electrolyze an aqueous suspension of an as-manufactured C.I. Sulfur Black 1 press-cake. The reaction is started with 337 g of C.I. Sulfur Black 1 reckoned dry in 4 L of water comprising 16 mL of 50% aqueous sodium hydrosulfite solution and continued up to an amount of 1740 g of C.I. Sulfur Black 1 reckoned dry in a total volume of 6.81 L. By gradually, over a period of 1320 minutes, adding portions of 126 g to 253 g of C.I. Sulfur Black 1 reckoned dry. The electrolysis is begun at a current density of 0.83 mA/cm² and continued at up to 100 mA/cm², with increasing leuco dye concentration, using a flow velocity of 0.2 m/s.

[0053] The level of reducing equivalents which is ascertainable after the electrolysis is 5.67, which corresponds to a charge quantity of 504 Ah per kg of dye. The solution thus obtained has the same molecular composition as the dye solution produced in Production Example 1.

[0054] The HPLC spectrum of the reaction product is reproduced in FIG. 1.

[0055] The reaction product can be isolated as a solid material as follows:

Variant 1:

[0056] The dye solution is heated to 130°C and is maintained at 130°C. For 12 hours until a dry residue is present. 34 g are isolated of a dry black product which is readily and completely soluble in water and can be used for dyeing.

Variant 2:

[0057] 100 g of the leuco dye solution are admixed with carbon dioxide at 60°C. Until the pH is ≤ 9 and the dye has fully precipitated. The precipitated dye is filtered off under argon and dried at 80°C. Under reduced pressure. 22 g are isolated of a dry black product which is readily and completely soluble in dilute aqueous sodium hydrosulfite solution and can be used for dyeing.

PRODUCTION EXAMPLE 5 (SAMPLE 6)

[0058] A flowthrough cell divided by a cation exchange membrane (Nafion 424) is used to electrolyze an aqueous suspension of an as-manufactured C.I. Vat Blue 43 press-cake, the reaction being started with 500 g of C.I. Vat Blue 43 reckoned dry in 3 L of water comprising 8 mL of 50% aqueous sodium hydrosulfite solution and 4 mL of Primasol NF wetting agent. This amount is gradually raised to 400 g of C.I. Vat Blue 43 reckoned dry in a total volume of 4.6 L. The electrolyte is used aqueous sodium hydrosulfite solution (1 mol/L). The electrolysis is conducted over 650 minutes using a current density of 100 mA/cm² coupled with a flow velocity of 0.2 m/s. The level of reducing equivalents which is ascertainable after the electrolysis is 3, which corresponds to a charge quantity of 2205 Ah per kg of dye. The solution thus produced can be used for dyeing purposes either without further additions or with minimized additions of reducing agents.
The HPLC spectrum of the reaction product is reproduced in FIG. 6.

Isolation as a Solid Material:

100 g of the dye solution are admixed with carbon dioxide at 600C until the pH is <9 and the dye has fully precipitated. The precipitated dye is filtered off under argon and dried at 80° C. under reduced pressure. 15 g are isolated of a dry deep blue product which is readily and completely soluble in dilute aqueous sodium hydroxide solution and can be used for dyeing.

PRODUCTION EXAMPLE 6 (SAMPLE 7)

A flowthrough cell divided by a cation exchange membrane (Nafon 424) is used to electrolyze C.I. Vat Blue 43 suspension at a current density of 10 mA/cm² as described in EP 101222104.

The HPLC spectrum of the reaction product is reproduced in FIG. 7.

PRODUCTION EXAMPLE 7

100 g of a Leuco Sulfur Black 1 solution having a dye concentration of 330 g/L, the solution having been prepared in accordance with Production Example 4 of the DE 102004040601.4 application, is heated to 130° C. and maintained at 130° C. for 12 hours until a dry residue is present. 34 g are isolated of a dry black product which is readily and completely soluble in water and can be used for dyeing.

PRODUCTION EXAMPLE 8

100 g of a Leuco Sulfur Black 1 solution having a dye concentration of 330 g/L, the solution having been prepared in accordance with Production Example 4 of the DE 102004040601.4 application, are admixed with carbon dioxide at 60° C. until the pH is <9 and the dye has fully precipitated. The precipitated dye is filtered off under argon and dried at 80° C. under reduced pressure. 22 g are isolated of a dry black product which is readily and completely soluble in dilute aqueous sodium hydroxide solution and can be used for dyeing.

PRODUCTION EXAMPLE 9

100 g of a solution of reduced C.I. Vat Blue 43 having a dye concentration of 250 g/L, the solution having been prepared in accordance with Production Example 5 of the DE 102004040601.4 application, are admixed with carbon dioxide at 60° C. until the pH is <9 and the dye has fully precipitated. The precipitated dye is filtered off under argon and dried at 80° C. under reduced pressure. 15 g are isolated of a dry deep blue product which is readily and completely soluble in dilute aqueous sodium hydroxide solution and can be used for dyeing.

Dyeings

Dyeing in Conventional Exhaust Process

A dyeing liquor containing 16% in the case of C.I. Sulfur Black 1 and 10% in the case of C.I. Vat Blue 43 of leuco dye solution produced according to Production Examples 1-5, 2 g/l of anionic wetting agent, 2 ml/l of 38° Be caustic soda, 10 ml/l of Sulphhydrate Ê 150%, 5 ml/l of Stabilisal S liq., 30 g/l of sodium sulfate and about 50 ml of completely ion-free water, so that the total liquor is 100 ml, is used to bleach a cotton fabric, for example a loop-formingly knitted cotton fabric, in an exhaust process at a liquor ratio of 10:1 starting at an initial temperature of 50° C., heating to 95° C. at 2°/minute, then dyeing at 95° C. for 45 minutes and subsequently cooling to 60° C. at 30° C/minute. By way of aftertreatment, the fabric is rinsed for about 5 minutes with cold completely ion-free water and then reoxidized. To this end, the dyed fabric is treated, in a liquor ratio of 1:1, with 1% of hydrogen peroxide 35% and 2% of acetic acid at a pH of 4.5 at 70° C. for 15 minutes. The oxidation to the solid sulfur dye can alternatively also be effected by blowing air in at 60° C. for two hours.

The dyed fabric is subsequently rinsed in hot completely ion-free water for 3 to 5 minutes and then in cold completely ion-free water for up to 5 minutes, squeezed off and dried.

Electrochemical Dyeing

A cell divided by a cation exchange membrane and having a capacity of 25 ml, having a 3-ply cylindrical stainless steel-cathode having a total surface area of 2 m², a stainless steel mixed oxide coated titanium electrode and also 0.1M NaOH as anolyte and catholyte containing 540 g of C.I. Sulfur Black 1 as a 33% moist paste, 52 ml of wetting agent, 210 ml of 50% aqueous sodium hydroxide solution and also 1.56 kg of NaCl is used to carry out an electrolysis where the initial phase involves a reduction at a cell current of 25 A, a cell voltage of 25 V at about 8 volts at a current density of 125 mA/cm². In the process, the dyebath is circulated at about 55 l/kg through the motor to be dyed, a metric count 69 cotton yarn package having a mass of 2700 g and having been pretreated to be ready for dyeing, and pumped as a bleed stream through the cathode space, so that the dyebath is continually regenerated through exchange with the catholyte.

The dyeing program consists of a plurality of phases:

1. reducing and heating phase: during this phase the dyebath is brought to the requisite dyeing temperature while at the same time the requisite current density for dye reduction is applied.

2. dyeing and cooling phase: the actual dyeing process is carried out at 80° C.

3. completion: oxidation with hydrogen peroxide, rinsing and drying.

The dyeing obtained in this way has an I value of 27.11, an s value of +0.66 and a b value of –1.95.

1. Leuco sulfur dye compositions obtainable at current densities between 50 mA/cm² and 500 mA/cm² and a flow velocity in the range from 0.1 m/s to 2 m/s.

2. The leuco sulfur dye compositions according to claim 1 which are obtainable at current densities between 50 mA/cm² and 150 mA/cm² and a flow velocity in the range from 0.1 to 0.4 m/s.

3. Mixtures of different leuco sulfur dye compositions according to claim 1.

4. A process for producing leuco sulfur dye compositions according to claim 1, which comprises starting at a concentration of 20 g/l and an initial current density of 0.5 mA/cm².
and continuously increasing the concentration to 600 g/l and
the current density to 500 mA/cm².

5. The process for producing leuco sulfur dye compositions
according to claim 4 which further comprises adding
catalytic amounts of Bunte salts of the general formula
R-S-SO₄Na, where R represents organic repeat structural
elements, or by catalytic addition of chemical reducing
agents.

6. The process according to claim 4 wherein a massive
plate electrode or a three-dimensional electrode is utilized in
a divided electrolytic cell.

7. The process according to claim 4 wherein alkaline
solutions of alkali metal salts are used as conducting elec-
trolyte.

8. The process for producing leuco sulfur dye compositions
according to claim 4 wherein electrolysis is effected at
temperatures in the range from 20 to 135° C.

9. The process for producing leuco sulfur dye compositions
according to claim 4 wherein electrolysis is effected at
temperatures in the range from 20 to 95° C.

10. The sulfur dye compositions according to claim 1
wherein the sulfur dye is quinoneimine and wherefor a
concentration of reduction equivalents between 75 Ah/kg
and 225 Ah/kg based on 1 kg of dry solid dye is present
when C.I. Vat Blue 43 is used as dye raw material.

11. The process for producing reduced quinoneimine
sulfur dyes in their solid form by lowering the pH to ≤ 9
and/or drying the electrochemically reduced leuco quinone-
imine sulfur dye solutions.

12. The sulfur dye compositions according to claim 1
wherein the sulfur dye is quinoneimine and wherefor a
concentration of reduction equivalents between 75 Ah/kg
and 225 Ah/kg based on 1 kg of dry solid dye is present
when C.I. Vat Blue 43 is used as dye raw material.

13. Dye preparations comprising leuco sulfur dye com-
positions according to claim 1.

14. Solid dye preparations comprising leuco sulfur dye
compositions having a water content ≤ 5% by weight based
on the entire product.

15. A process for dyeing and printing cellulosic material,
which comprises utilizing leuco sulfur dye compositions
according to claim 1.

16. A process for dyeing cellulosic material, which
comprises effecting the electrochemical reduction to produce
leuco sulfur dye compositions according to claim 1 directly
in the dyebath.

17. (canceled)

18. The process for producing leuco sulfur dye compos-
tions according to claim 4 which further comprises adding
catalytic amounts of Bunte salts of the general formula
R—S—SO₄Na, where R represents phenothiazine, thia-
zone, thiouylene or phenoazoate substructures, or by cata-
lytic addition of chemical reducing agents which are
selected from the group consisting of sodium dithionite,
organic sulfonic acids, organic sugars and mixtures thereof.

19. Solid dye preparations according to claim 14 com-
prising leuco sulfur dye compositions having a water content
≤ 2% by weight based on the entire product.

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