Process and Apparatus for the Electrolytic Reduction of Sulfur Dyes

Introduction

The present invention concerns a process for the electrolytic reduction of sulfur dyes, comprising the steps of providing an aqueous catholyte comprising at least one sulfur dye, providing an electrolytic cell with an anode disposed in an anolyte in an anolyte compartment, a cathode disposed in a catholyte in a catholyte compartment and an electrochemical separator between anolyte compartment and catholyte compartment and applying a potential between the anode and the cathode which is above the value at which hydrogen is generated, characterized in that the catholyte does not comprise any inorganic or organic reduction agents. The invention further concerns an Apparatus for the application of that process and the use of an electrolytic cell for the reduction of dye liquor comprising sulfur dyes.

Prior art

Sulfur dyes are the most common dyestuff class in the denim industry apart from indigo. Sulfur dyes are commercially available in pre-reduced liquid form or as oxidized powder product. Only the reduced form (leuco form) of sulfur dyes has a sufficient affinity and fixation to textile materials especially to cellulosic fibers. The reduction of sulfur dyes is usually carried out with inorganic or organic reduction agents like polysulfide products, glucose or others.

During the dyeing process some reduced dyestuff is undesirably oxidized, for example by air that is introduced into the dye bath by the textile material or by ambient air. The oxidized dye accumulates in the dye bath unless it becomes re-reduced. This reduction is commonly achieved by reduction agents, which are continuously dosed into the dye bath. The addition of the conventional reduction agents lead to increased costs in waste water treatment and to

problems in complying with environmental laws, because the reaction products of the reduction agents remain in the used dye bath and are therefore present in the waste water.

Electrochemical reduction of sulfur dyes is known for examples from US 3,640,803 A. The cathode potential is below the value at which a noticeable quantity of hydrogen is generated. In fact, care is taken, that no hydrogen evolves by using cathodes with a high hydrogen overvoltage and by termination of the process when hydrogen evolves. The voltage used is stated to be 3 to 6 V. This process refers to an electrolytic cell open to ambient atmosphere.

US 6,627,063 B1 discloses a method for the reduction of dyes including sulfur dyes in aqueous solutions for the use in a dyeing procedure. The reaction has to be started either by addition of reducing agents or by UV irradiation. The latter results in a slow start of the reaction. Development of hydrogen during the process is not disclosed. The highest voltage disclosed is 2.6 V.

It is the purpose of the present invention to eliminate or at least to reduce the amount of reducing agents used in dyeing processes using sulfur dyes. It is further a purpose of the present invention to improve overall efficiency of the electrolytic reduction process and especially to improve space-time yield. It is further a purpose of the present invention to reduce sulfur dyes in high concentration using both electrolytic reduction as well as hydrogen generated during the process.

Description of the present invention

The first embodiment of the present invention is a process for the electrolytic reduction of sulfur dyes, comprising the steps of

- providing an aqueous catholyte comprising at least one sulfur dye,

- providing an electrolytic cell with an anode disposed in an anolyte in an anolyte compartment, a cathode disposed in a catholyte in a catholyte compartment and an electrochemical separator between anolyte compartment and catholyte compartment
- applying a potential between the anode and the cathode which is above the value at which hydrogen is generated,

wherein the catholyte does not comprise any inorganic or organic reduction agents.

This invention has the advantage that no reducing agent is used in the reduction of sulfur dyes. This sharply reduces the environmental problems usually accompanied with the dyeing process, since the materials used are not or much less problematic with respect to the environment. The high voltage allows for an efficient reduction and a smaller electrolytic apparatus than would be necessary when using a voltage at which no hydrogen is produced. The present process has significant advantages in the efficiency of the reduction process. The recovery of expensive or environmentally harmful materials (e.g., reducing agent, mediator system) becomes unnecessary. The wording "wherein the catholyte does not comprise any inorganic or organic reduction agents." does not exclude the leuco sulfur dye from being present in the catholyte.

In the present process, it is important to provide an excess potential to the electrodes, otherwise hydrogen will not be generated and an efficient reduction of the sulfur dye would not be realized. Surprisingly, an intensive formation of hydrogen gas in the presence of oxidized sulfur dye cannot be observed. The reduction of the dye by the hydrogen produced happens instantly. By the instant reduction of the hydrogen the formation of mixtures of oxygen with hydrogen is avoided, which carries the risk of explosions. A process of the present invention where the catholyte compartment has no contact to the ambient atmosphere is therefore preferred. Preferred is also a process of the present invention where the potential of the electrodes and the current through

the electrodes are limited such that accumulation of gaseous hydrogen above the catholyte is avoided.

Sulfur dyes cannot be used for dyeing in their normal oxidized form. For the dyeing process they have to be converted to their reduced form (leuco form) by reducing agents or by electrolysis. As described above, a part of the reduced dyestuff is undesirably oxidized during the dyeing process, resulting in changes of color tone, hue and other properties of the textile materials dyed during the live time of a dye bath. To prevent such disadvantages, usually the oxidized form of the sulfur dyes is re-reduced by reducing agents. These reducing agents lead to wastewater problems. Preferred is therefore a process as described herein, wherein the catholyte is a dye liquor comprising sulfur dyes. In the present text the term dye liquor refers to a liquid used in a dye bath or that can be used in a dye bath. Usual dye liquors of sulfur dyes are well suited as catholyte in the present process. The dye concentrations, electrolyte concentrations and pH values of the dye liquors allow their direct reduction at a cathode without further changes. The dye liquors may therefore be used without alteration in the present process. Addition of reducing agents or salts that improve conductivity is not necessary.

Preferred is a process as described herein, wherein the catholyte is circulated between a secondary liquor vessel and the catholyte compartment. Especially preferred is a process as described herein, wherein the catholyte is a dye liquor comprising sulfur dyes and wherein the dye liquor is circulated between a dye bath in a dyeing range and the catholyte compartment. This allows to replenish continuously the dye bath with re-reduced dye liquor without interruption of the dye process and without addition of undesired chemicals. In a continuous operation, usually except for dye and alkali hydroxide or another a base and possibly only a very small amount of additives, like surfactants, wetting agents, dispersing agents or the like, no other chemicals effective in the oxidation-reduction process are used.

Sulfur dyes preferred for the use in the present process are described for example in the Color Index published by the British Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists. Especially preferred examples of such dyes are the leuco forms C.I. Sulfur Black (e.g. C.I. Sulfur Black 1, C.I. Sulfur Black 76), C.I. Sulfur Blue (e.g. C.I. Sulfur Blue 2, C.I. Sulfur Blue 5, C.I. Sulfur Blue 15), C.I. Sulfur Brown (C.I. Sulfur Brown 7, C.I. Sulfur Brown 8, C.I. Sulfur Brown 21, C.I. Sulfur Brown 52), C.I. Sulfur Green (e.g. C.I. Sulfur Green 3), C.I. Sulfur Orange (e.g. C.I. Sulfur Orange 1), C.I. Sulfur Red (C.I. Sulfur Red 1, C.I. Sulfur Red 6). Most preferred is C.I. Leuco Sulfur Black 1.

The present process is preferably conducted with an anolyte or a catholyte that has a pH value in the range of from 9 to 14. Preferably both, anolyte and catholyte have a pH value in that range. At such a pH, the leuco sulfur dyes have a good solubility and the catholyte (or dye liquor) has sufficient conductivity to allow for an efficient electrolysis. In addition the power efficiency for the electrolysis of water in alkaline aqueous media is known to be very high, i.e. up to 90%. The pH is preferably adjusted by addition of an alkaline substance, e.g. alkali metal hydroxides. Preferred is the use of sodium hydroxide and/or potassium hydroxide. Most preferred is the use of sodium hydroxide. Also preferred is a process as described herein, wherein the anolyte and the catholyte independently comprises alkaline substances in a concentration in a range of from 0.001 mol per liter to 1 mol per liter, preferably in a range of from 0.01 to 0.5 mol per liter.

As material for anode and/or cathode the usual electrode material can be used, such as platinum, titanium, nickel, graphite or stainless steel in form of a foam or a flat electrode. The material should be stable at a pH value of 9 to 14. The distance between anode and cathode including the electrochemical separator in between is preferably in a range of from 2 mm to 100mm. In a preferred process of the present invention, the current density is in a range of from 100 to 5000 mA/cm^2, preferably of from 100 to 2000 mA/cm^2 and more preferably 300 to 800 mA/cm^2. These parameters allow for a sufficient reduction capacity as

usually necessary for the reduction, especially for the continuous reduction in a circular process, of a catholyte in general or a dye liquor.

It is important to provide an excess potential to the electrodes, otherwise hydrogen will not be generated and a sufficient reduction of the sulfur dye would not be realized. The potential (voltage) between the anode and cathode is preferably at least 5 V, at least 7 V or at least 10 V. It is more preferably at least 12 V and most preferably at least 15 V. A high potential allows for optimization of the space-time yield of the electrolytic cell. The diffusion of the insoluble sulfur dye or the partially reduced leuco sulfur dye is not anymore the limiting step for the reaction rate. In the present process the presence of water on the cathode surface is sufficient to effect reduction of water to hydrogen. The present invention therefore allows the use of a comparatively small electrolytic apparatus, preferably comprising a closed electrolytic cell for the reduction of the sulfur dyes. Therefore, the process is useful both for the reduction of sulfur dyes in high concentration (preferably a concentration of 20%-50% w/w) and for the re-reduction of sulfur dyes in dye liquors (dye baths), which usually have a relatively low combined concentration of dye and leuco dye, e.g. 50 g/L or lower or even 20 g/L or lower of sulfur dye in the catholyte. The concentration of the sulfur dye itself in the dye bath is often even much lower than this.

A further way of reduction of the sulfur dye besides the direct transfer of electrons from the cathode to the oxidized form of the sulfur dye and the reduction by hydrogen is the reduction by the leuco sulfur dye. Sulfur dyes have the ability to achieve several reduction states between the oxidized form and the fully reduced sulfur dye. Fully reduced leuco sulfur dye or leuco sulfur dye of a high reduction state (i.e. strongly reduced) may react with the oxidized form of the sulfur dye or with leuco sulfur dye in a low reduction state (i.e. not strongly reduced) in a comproportionation reaction to yield a leuco sulfur dye of a medium reduction state. Leuco sulfur dye that is present in the catholyte in a reduction state different from the fully reduced leuco sulfur dye may also be further reduced by direct electron transfer from the cathode or by hydrogen

during the process of the present invention. The leuco sulfur dye with a high reduction state thus produced may then reduce the oxidized form of the sulfur dye in a comproportionation reaction.

To improve convection the catholyte in the cathode compartments is agitated by stirring or the like. It is however sufficient for a circular process as described herein when the construction of the cathode compartment results in a steady flow of the catholyte through the cathode compartment. This may have the same effect as stirring or the like.

In the process of the present invention the catholyte has preferably a temperature in a range from 0 to 100°C, more preferably in a range from 15 to 95°C, even more preferably in a range from 50 to 95°C and most preferably in a range from 70 to 90°C.

In an especially preferred process according to the present invention at least 50% of the reduction of the sulfur dye is achieved by hydrogen created at the cathode. This allows for a sufficient reduction capacity with high efficiency. For the purposes of this invention for a given system the current at which 50% of the reduction of the sulfur dye is achieved by hydrogen created at the cathode is determined as follows:

i. For the electrolytic cell comprising anolyte and catholyte, but no sulfur dye or leuco sulfur dye in the catholyte, the highest voltage is measured at which no hydrogen is produced.
ii. To the same electrolytic cell comprising anolyte and the complete catholyte, the potential measured in step i is applied between the electrodes and the current is measured.
iii. The current at which 50% of the reduction of the sulfur dye is achieved by hydrogen created at the cathode is twice the current measured in step ii.

The electrolytic cell is divided into an anode half-cell and a cathode half-cell by an electrochemical separator so that re-oxidation of the dyestuff cannot occur at the anode. The separator can be a diaphragm or a semipermeable membrane. Preferred is a process wherein the electrochemical separator is a semipermeable membrane that allows passage of protons and prevents passage of oxygen, hydrogen, sulfur dye and leuco sulfur dye. It is further preferred that the electrochemical separator is a cation permeable membrane, more preferably a cation exchange membrane and even more preferably a proton exchange membrane.

In case the electrochemical separator comprises or is a membrane, the preferred membranes are substantially chemically stable to the process conditions and mechanically and chemically suitable for the design and economical operation of the electrolytic process. It is preferred that the membrane comprises an ionomer. It is also preferred that the membrane comprises hydrocarbon polymers and/or halocarbon polymers comprising at least one acidic functional group or their salts. Most preferred are pendant functional groups selected from the group comprising sulfonic acid groups, pendant sulfonamide groups and pendant carboxylic acid groups. In the process as described herein the use of fluorinated carbon polymers, preferably perfluorinated carbon polymers is most preferred. Best suited are electrochemical separators comprising a membrane comprising or consisting of a polymer with a polytetrafluoroethylene backbone and sulfonic acid groups or theirs salts. Nafion™ and RTM™ are especially useful materials for the process according to this invention. Any of the acidic groups of the materials mentioned herein may also be present in form of their salts.

A further embodiment of the present invention concerns an apparatus for the electrolytic reduction of sulfur dyes, comprising

- an electrolytic cell with an anode, a cathode, an anolyte compartment, a catholyte compartment and an electrochemical separator between anolyte compartment and catholyte compartment

- a secondary liquor vessel
- an aqueous catholyte comprising at least one sulfur dye
- a pump or pumps for circulating the catholyte between the secondary liquor vessel and the catholyte compartment.

In a preferred embodiment of the apparatus, the secondary liquor vessel is a dye bath in a dyeing range and the catholyte is a dye liquor.

Preferably the electrochemical separator is a cation permeable membrane, preferably a cation exchange membrane and more preferably a proton exchange membrane. Preferably the apparatus is equipped with a DC electric power supply that allows applying a potential between the anode and the cathode which is above the value at which hydrogen is generated. The apparatus also preferably is equipped as described above in regard to the process of the present invention with the same embodiments and preferred embodiments for the anode, cathode, electrochemical separator, anolyte, catholyte and/or dye liquor. In a further preferred embodiment the apparatus has a potential between anode and cathode of at least 5 V, preferably at least 7 V, more preferably at least 10 V, even more preferably at least 12 V and most preferably at least 15 V

A further embodiment of the present invention concerns the use of an electrolytic cell for the reduction of a dye liquor comprising sulfur dyes. Preferred is the use at a potential between anode and cathode of at least 5 V, preferably at least 7 V, more preferably at least 10 V, even more preferably at least 12 V and most preferably at least 15 V. Further preferred is the aforementioned use comprising the use of any apparatus as described herein in connection with any process of the present invention.

Examples:

Example 1

Continuous pre-dyeing of cotton yarn with C.I. Leuco Sulfur Red 11 on an indigo slasher dyeing range:

textile material:	cotton yarn
yarn count:	Ne 10 (8,400 yards/lb. yarn)
number of ends:	4,260
range speed:	25 m/min
dye concentration:	10 g/L C.I. Leuco Sulfur Red 11
dye bath volume:	1,750 liter including electrolytic cell
number of dyeboxes:	1
dyefeed:	44 g/min C.I. Leuco Sulfur Red 11

The electrolytic cell was connected to a pre-dyeing box of an indigo dyeing range. A split-type electrolytic cell was used, i.e. the anode and cathode half-cells were separated by a Nafion PFSA membrane (commercially available from DuPont). As anode a 4-ply titanium electrode was used, as cathode a 4-ply stainless steel electrode.

The anolyte was a 0.01N NaOH solution, in which the alkaline concentration was kept stable by an automatic dosing system.

The catholyte was a dye solution of 10 g/L C.I. Leuco Sulfur Red 1, NaOH (pH 12.0), 2 g/L of a commercial wetting agent (BluWet) and 2 g/L of a commercial dispersing agent (BluSperse). The temperature of the dye solution was 80°C. The electrolysis was carried out with a current density of 500 mA/sqcm and 17 V.

For the pre-dyeing process the cotton yarn passed the pre-dyeing box, which is connected to the electrolytic cell, both containing the dyeing liquor with the sulfur dye, which is circulated between the two compartments. Afterwards the textile material passed 2 rinsing boxes with water and then was overdyed with indigo in the usual way.

No increase of the ORP (oxidation-reduction-potential) of -660 mV - measured with a platinum electrode - was observed during the whole dyeing process of 7500 m yarn.

The textile material was continuously overdyed with indigo in the usual way. After the dyeing process all of the dyed yarn showed the same shade and the same depth of shade, which is a clear indication that all of the sulfur dye in the dye bath was reduced at any time during the process.

Example 2

Reduction of a sulfur dye in high concentration

The same electrolytic cell as in Example 1 was used.

dye: sulfur black 1 powder
dye concentration: 300g/l
caustic concentration (NaOH): 0.4 mol /l
total volume: 2 liter
density: 600 mA/sqcm
potential: 12 V
temperature: 80°C

The dye liquor was circulated between a preparation flask and closed electrolytic cell continuously. After 30 minutes reduction potential stabilized at more than -660 mV indication that the entire dyestuff present was reduced. This was confirmed by a spot test.

Claims

1. Process for the electrolytic reduction of sulfur dyes, comprising the steps of

   - providing an aqueous catholyte comprising at least one sulfur dye,
   - providing an electrolytic cell with an anode disposed in an anolyte in an anolyte compartment, a cathode disposed in a catholyte in a catholyte compartment and an electrochemical separator between anolyte compartment and catholyte compartment
   - applying a potential between the anode and the cathode which is above the value at which hydrogen is generated,

   wherein the catholyte does not comprise any inorganic or organic reduction agents.

2. A process according to claim 1, wherein the catholyte is a dye liquor comprising sulfur dyes.

3. A process according to claim 1 or 2, wherein the catholyte is circulated between a secondary liquor vessel and the catholyte compartment.

4. Process according to any of the preceding claims, wherein the anolyte and/or the catholyte have a pH value in the range of from 9 to 14.

5. Process according to any of the preceding claims, wherein the anolyte and the catholyte independently comprise alkaline substances in a concentration in a range of from 0.001 mol per liter to 1 mol per liter, preferably in a range of from 0.01 to 0.5 mol per liter.

6. A process according to any of the preceding claims, wherein the current through the electrodes is in a range of from 100 to 5000 mA/cm^2, preferably of from 300 to 800 mA/cm^2.

7. Process according to any of the preceding claims, wherein the potential between the electrodes is at least 5 V, preferably at least 7 V, more preferably at least 10 V, even more preferably at least 12 V and most preferably at least 15 V.

8. Process according to any of the claims 1 to 6, wherein at least 50% of the reduction of the sulfur dye is achieved by hydrogen created at the cathode.

9. Process according to any of the preceding claims, wherein the electrochemical separator is a cation permeable membrane, preferably a cation exchange membrane and more preferably a proton exchange membrane.

10. Process according to any of the preceding claims, wherein the electrochemical separator comprises a membrane comprising hydrocarbon polymers and/or halocarbon polymers which comprise pendant functional groups selected from the group comprising sulfonic acid groups, pendant sulfonamide groups and pendant carboxylic acid groups.

11. Apparatus for the electrolytic reduction of sulfur dyes, comprising

- an electrolytic cell with an anode, a cathode, an anolyte compartment, a catholyte compartment and an electrochemical separator between anolyte compartment and catholyte compartment
- a secondary liquor vessel
- an aqueous catholyte comprising at least one sulfur dye

- a pump or pumps for circulating the catholyte between the secondary liquor vessel and the catholyte compartment.

12. Apparatus according to claim 11, provided with an anode, a cathode, an electrochemical separator, an anolyte, a catholyte, a dye liquor and/or a secondary liquor vessel according to any of the claims 1 to 10.

13. Use of an electrolytic cell for the reduction of a dye liquor comprising sulfur dyes at a potential between anode and cathode, which is above the value at which hydrogen is generated.

14. Use according to claim 13, wherein an apparatus according to any of claims 11 or 12 is used.

15. Use according to claims 13 or 14, wherein an anode, a cathode, an electrochemical separator, an anolyte, a catholyte and/or a dye liquor according to any of the claims 1 to 11 are used.