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(54) Title: PH CONTROL IN A DYEING PROCESS USING CO₂

(57) Abstract: The present invention is generally related to a dyeing process for a textile substrate, and in particular, related to a dyeing process using CO₂ to control pH, especially pH of a textile substrate in the pretreatment stage.



pH control in a dyeing process using CO₂

Field of the Invention:

The present invention is generally related to a dyeing process for a textile substrate, and in particular, related to a dyeing process using CO₂ to control pH, especially pH of a textile substrate in the pretreatment stage.

Background of the Invention:

A conventional textile dyeing process is generally divided into stages of pretreatment, dyeing, printing, and finishing. Pretreatment of a textile is performed in order to remove natural impurities and artificial impurities from textile fabrics and to improve the uniformity, hydrophilic characteristics, and affinity for dye stuffs. The pretreatment stage generally includes steps of singeing, de-sizing, scouring, bleaching, mercerizing, etc. A lot of auxiliary agents are used in the pretreatment process. For example, the scouring and bleaching of a textile fabric is generally carried out under alkaline conditions, and in mercerization of a textile fabric, especially a cotton fabric, the fabric is treated in a 20% caustic soda solution. If washing is not sufficient, residues of the alkaline agents often remain in the textile fabric after pretreatment. It is known that pH has a great effect on dye uptake in the dyeing process, and it is important to control pH in the dyeing process.

The dyeing stage of a textile is often carried out in a dyeing solution. The dyeing solution must also maintain a proper pH to provide accurate and uniform shading of color.

In the prior art, acetic acid (CH₃COOH) is widely utilized in different stages of a dyeing process for pH control. However, CH₃COOH, as one kind of organic acids, is quite expensive. Besides, CH₃COOH gives off pungent smell, is harmful for eyes and skin of workers, and increases COD (chemical oxygen demand) for the waste stream which is not easy to treat.

Therefore, there exists a need for seeking a new cost-effective, environmental friendly and efficient method to maintain and control pH, that obviates the use of acetic acid in the dyeing process, especially in the pretreatment stage of the dyeing process.

Summary of the Invention:

In one aspect, the present invention provides a method of controlling pH of a textile substrate in pretreatment stage of a dyeing process, the method comprising the steps of:

- providing a carbonic acid solution; and

- introducing the carbonic acid solution to a dye vat containing the textile substrate, to control the pH of the textile substrate to be around neutral, for example, 6.5-7.5.

In a further aspect, the present invention provides a method of controlling pH of a dyeing solution in a dyeing process, the method comprising the steps of:

- providing a carbonic acid solution;

- providing a dyeing solution in a dye vat; and

- adding the carbonic acid solution to the dyeing solution in the dye vat, to control the pH of the dyeing solution.

According to the present invention, the carbonic acid solution is prepared by delivering carbon dioxide (CO_2) gas into water in a pressurized reactor system and mixing with water under elevated pressure. Carbon dioxide and water form carbonic acid, which dissociates into bicarbonate and hydrogen ions. Depending on the concentration of carbonic acid, the solution will have different pH, which is normally expected to be 5-7, and at that pH carbonic acid is in equilibrium with dissociated bicarbonate ions and hydrogen ions in water.

In one embodiment of the present invention, the prepared carbonic acid solution is added to a dye vat containing pretreated textile substrate. Upon adding the carbonic acid solution in the dye vat, the hydrogen ions in the carbonic acid solution react with alkaline agent remained and adsorbed in the pretreated textile substrate, to reduce the pH of the textile substrate.

The concentration of the carbonic acid solution can be adjusted and determined by a skilled person in the art depending on the textile substrate to be treated, and is generally 0.2 to 5 g/l, preferably 0.5 to 3 g/l.

In another embodiment of the present invention, the prepared carbonic acid solution is added to a dye vat containing a dyeing solution. Upon adding the carbonic acid solution to the dyeing solution, hydrogen ion concentration increases, thereby reducing the pH of the dyeing solution. In addition, as a

buffering system, bicarbonate and carbonate ions can be formed in the carbonic acid solution, and maintain the pH of the dyeing solution.

Unlike a conventional method which injects CO₂ gas to a dyeing process through a sparger or through direct gas injection into the vat atmosphere, the present invention employs CO₂ in the form of a carbonic acid solution which is prepared separately by pre-dissolving CO₂ gas in water in a reactor system, and the resulting carbonic acid solution is delivered to the dye vat via a pump. In a preferred embodiment, CO₂ gas can be additionally injected into the atmosphere in the dye vat to pressurize the dye vat, maintain the pressure of dye vat higher than atmospheric pressure but under the safety pressure of the vat, so as to prevent CO₂ from vaporizing from carbonic acid solution, and thus maintain carbonic acid concentration in the solution

By replacing CH₃COOH with CO₂ to control pH in the dyeing process, the present invention provides a lower operational cost and safer working environment for workers.

Further, by pre-dissolving CO₂ into water in a pressurized reactor system to obtain a carbonic acid solution, the present invention can achieve extremely high levels of CO₂ dissolution of > 95%, and high reaction efficiency.

Without wishing to be bound by theory, the inventor believes that when CO₂ gas is directly injected into a dye vat, from the viewpoint of a dynamic mass transfer process, CO₂ needs to be dissolved in water to generate carbonic acid, which then dissociates into hydrogen ions to react with alkali, and in this process, the step where the gas goes across the gas-liquid interface membrane controls the dissolution speed and is relatively slow, so the amount of CO₂ that can participate in the reaction is mainly affected by the step of gas dissolution. In contrast, if a carbonic acid solution is prepared in advance and added into the dye vat, the carbonic acid will directly react with the alkali after dissociation, without involving the slow step of two-phase mass transfer. As the reaction time in a dye vat is limited and the liquid level in a dye vat commonly used in the art is usually as shallow as less than 1m, the level of CO₂ dissolution can only be 50-70%, if CO₂ gas is directly injected into the dye vat via a sparger, especially when target CO₂ concentration is close to its solubility.

More importantly, the present invention allows the reactor system for

preparing a carbonic acid solution to be compatible with in-line or sidestream modes, and suitable for internal or external installation, and therefore, is adaptable to the existing different types of dyeing machines with a minimum structure modification needed.

Textile substrates suitable to be used in the present invention can be any known textile substrate in the art. Examples of suitable textile substrate include, but are not limited to, cotton, nylon, rayon, polyester, silk, wool, acrylic, leather, etc. The textile substrate to be employed in the present invention is preferably cotton.

Various types of natural and synthetic dyes can be used in the dyeing process of the present invention. Examples of dyes include, but are not limited to, acid, basic, reactive, disperse, direct, vat dyes.

The desired pH of a textile substrate after pretreatment stage is normally around neutral.

The desired pH of a dyeing solution in the dyeing process will depend on the type of dye and the textile substrate to be dyed. For example, the desired pH of a dyeing solution for a polyester substrate is 5.5-6, for a nylon substrate is 6-6.5, and for a cotton substrate is 6.5-7.

Brief Description of the Drawing

Fig. 1 is a schematic drawing of a pretreatment stage of a dyeing process using CO₂ to control pH of cotton cloth according to an embodiment of the present invention.

Detailed Description of the Preferred Embodiment

The present invention is further illustrated by the following examples, but is not limited to the scope thereof. Any experimental methods with no conditions specified in the following examples are selected according to the conventional method and conditions, or product or device specifications.

Example 1:

The dyeing process took place in an overflow dyeing machine.

A carbonic acid solution was prepared in a pressurized reactor system (SOLVOCARB® reactor available from Linde GmbH).

SOLVOCARB® reactor is a pressurized reactor which can dissolve CO₂

effectively into water by mixing CO₂ gas and water under pressurized conditions. Dye vats having a lot of different formats can be employed in the present invention, and in this Example, a typical overflow dyeing machine, in which the dyeing solution is pumped from the bottom of the vat, then goes through an external heat exchanger and sprays onto the cloth in the dyeing vat again from the top nozzles, was used.

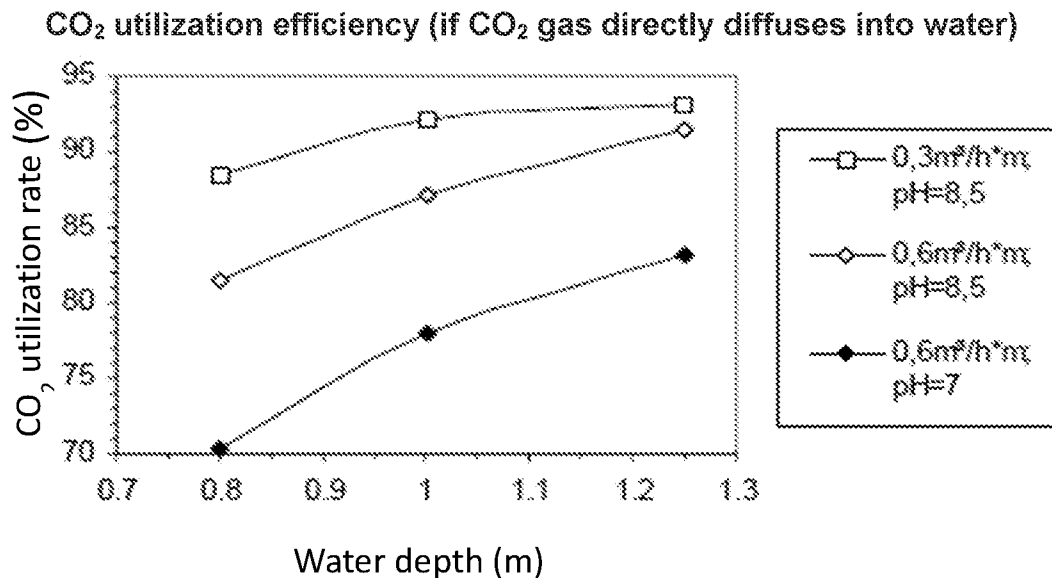
Fig. 1 shows a pretreatment process using carbonic acid solution to control the pH of cotton cloth.

As shown in Fig. 1, CO₂ gas was delivered into SOLVOCARB® reactor 1, and mixed with water under elevated pressure of 1 barg, to obtain 1 g/l carbonic acid solution.

In dye vat 2 of the overflow dyeing machine, cotton cloth was mixed with 2 g/l NaOH solution. The solution was heated to 98°C and maintained at this temperature for 60 min. Then the solution was removed and fresh water was added to the cloth, heated to 60°C and maintained at this temperature for 10 min. Then water was removed and 1 g/l carbonic acid solution as prepared above was added via a pump (which was not shown here), and washed the cloth for 10min. Then the solution was removed and fresh water was again added to the cloth, and washed for 10min. Finally water was removed and cloth was dried. After all these processing steps, the final pH of cloth was 6.5~7.5 and the cloth was ready for the next dyeing stage.

This example shows that carbonic acid solution can be used to effectively adjust the pH of a textile substrate in the pretreatment stage of a dyeing process, to achieve comparable technical effect with conventionally used acetic acid solution.

Further, CO₂ utilization efficiency was evaluated on a lab scale simulating the condition that CO₂ was directly injected and diffused into water in a dye vat. The result was shown in the following Figure. The CO₂ utilization efficiency was determined by employing a first method of measuring the volume of CO₂ gas escaped from water level and a second method of measuring the rising speed of CO₂ gas bubble in water and calculating in a model, and then taking an average of the values obtained from the first and second methods.



From the above Figure, it can be seen that CO₂ utilization rate is significantly affected by water depth. Considering the fact that water depth commonly used in the art is usually as shallow as <0.8m, at neutral pH CO₂ utilization rate would expect to be less than 70%, which is much less than CO₂ utilization efficiency of >95% for CO₂ pressurized vessel (SOLVOCARB® Reactor),.

The invention has been described herein in considerable detail in order to provide those skilled in the art with the information needed to construct and use embodiments of the invention as required. However, it is to be understood that various modifications can be accomplished without departing from the scope of the invention itself.

What is claimed is:

1. A process for dyeing a textile substrate, comprising in the pretreatment stage of the process, the steps of
 providing a carbonic acid solution;
 introducing the carbonic acid solution to a dye vat containing the textile substrate, to control the pH of the textile substrate to be around neutral.
2. The process for dyeing a textile substrate according to claim 1, wherein the carbonic acid solution is prepared in a pressurized reactor system.
3. The process for dyeing a textile substrate according to claim 1 or 2, further comprising the step of introducing additional CO₂ into the dye vat atmosphere to maintain carbonic acid concentration in the solution.
4. The process for dyeing a textile substrate according to any one of claims 1 to 3, wherein the carbonic acid solution has a concentration of 0.2-5 g/L.
5. The process for dyeing a textile substrate according to any one of claims 1 to 4, wherein the textile substrate is selected from the group comprising cotton, nylon, rayon, polyester, silk, wool, acrylic, and leather.
6. A process for dyeing a textile substrate, comprising the steps of:
 providing a carbonic acid solution;
 providing a dyeing solution in a dye vat;
 adding the carbonic acid solution to the dyeing solution in the dye vat, to control the pH of the dyeing solution.
7. The process for dyeing a textile substrate according to claim 6, wherein the carbonic acid solution is prepared in a pressurized reactor system.

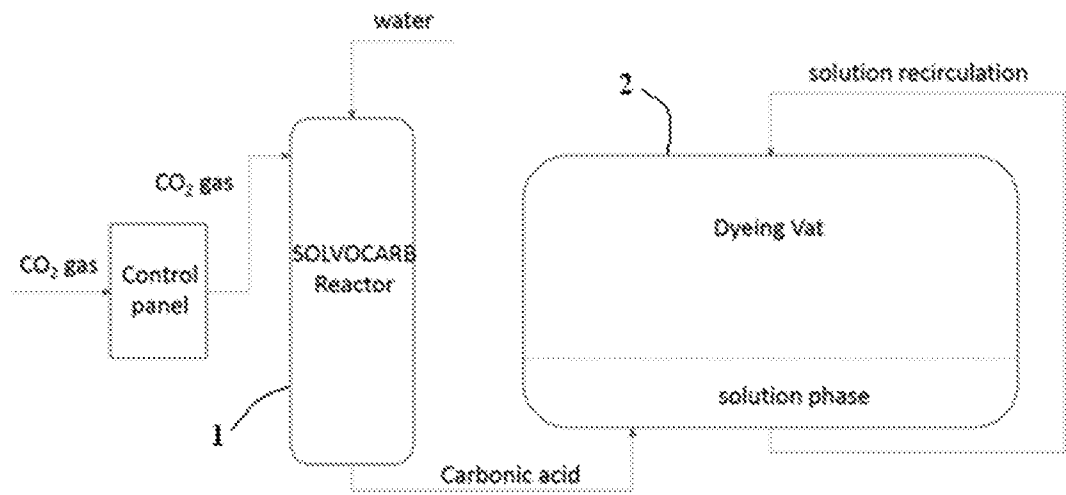


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/CN2022/076820

A. CLASSIFICATION OF SUBJECT MATTER INV. D06P1/653 D06P1/00 D06P1/673 D06P5/20 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) D06P		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 536 907 A (ZUMBRUNN JEAN-PIERRE [FR] ET AL) 27 August 1985 (1985-08-27)	1-5
Y	column 1, lines 5-10 column 2, lines 25-45 column 3, lines 9-52 column 4, lines 1-9, 35-61 column 5, line 5 - column 7, line 51; claims 10, 22 -----	6, 7
X	CN 107 780 239 A (HUZHOU NANXUN JINBAOJI TEXTILE CO LTD) 9 March 2018 (2018-03-09) paragraph [0006]; examples 1-3 -----	6, 7
Y	US 5 295 998 A (MERRITELLO RONALD J [US] ET AL) 22 March 1994 (1994-03-22) column 1, lines 5-10 column 4, lines 3-44 column 5, lines 20-21, 42-54; claim 1; examples 1-6 -----	6, 7
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
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Date of the actual completion of the international search 9 August 2022		Date of mailing of the international search report 22/08/2022
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Menard, Claire

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Information on patent family members

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