PRODUCTION OF COTTON WARP YARNS HAVING INVERSE DENIM EFFECT

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ABSTRACT
The present invention relates to a process for producing cotton warp yarns having an inverse denim effect, which comprises using an indigo dyeing range to perform

a dyeing step whereby the cotton warp yarn is through-dyed with indigo in one pass at a dyeing temperature of 30 to 90° C. and an indigo concentration of 5-500 g/l and

a subsequent bleaching step whereby the indigo is selectively decolorized on the surface of the cotton warp yarn.
PRODUCTION OF COTTON WARP YARNS
HAVING INVERSE DENIM EFFECT

[0001] The present invention concerns a process for producing indigo-dyed cotton warp yarns which have an inverse
denim effect and also textile articles comprising such cotton
warp yarns.

[0002] Denim refers to a relatively coarse woven cotton
fabric which was originally used for robust workwear, but
today is used particularly for manufacturing fashionable
jeans articles. The warp yarns needed to produce denim can
be dyed with indigo or else with sulfur dyes, especially
sulfur black, although dyeing to blue with indigo is greatly
predominant.

[0003] Traditionally, the warp yarn is dyed with indigo as
a rope or as a warp yarn sheet on specific dyeing ranges
which consist of a combination of one or more troughs with
squeeze rolls and a subsequent skying sector. The reduced
dye is applied in the troughs and oxidized in the skying
sector (see for example Technical Information T/T 017 d
from BASF AG dated June 1995, title: Continuous dyeing
with indigo).

[0004] The dyeing is typically carried out in a dyebath at
room temperature or slightly elevated temperatures of about
20-35° C., a pH of about 10.5 to 14 and an indigo concentra-
tion of about 0.5 to 10 g/l. Wetting agents in a concentra-
tion of 0.1 to 5 g/l can be used as well. A redox
potential in the dyebath is maintained by using an excess of
hydrosulfite reducing agent in amounts of about 0.1 to 5 g/l.
The yarn contact time with the dyebath is generally 8 to 30
seconds per pass. Dyeing in multiple passes, i.e., the
repeated application of dye from the dyebath by dipping
with subsequent squeezeoff in the dyeing trough and the
following skying, makes it possible to achieve deeper shades
(see for example ITB Veredlung 2/90, title: Indigo-Färberei:
Verfahrens- und maschinen- technische Lösungen, author: Dipl. Ing. L. Haas).

describes single-pass dyeing wherein, to overcome the low
affinity of indigo, the dyebath additionally has added to it
salt in the form of sodium chloride in order that an electro-
yte concentration of 200 to 350 g/l may be set.

[0006] These processes all produce a so-called ring dye-
ing, i.e., the fiber is dyed at the surface only, leaving the
interior of the fiber, the core, undyed. Ring dyeing makes it
possible to endow made-up denim articles with a high-
contrast appearance in particular washing and/or bleaching
processes through a wash-down of the initially dark blue
fabric. An example is the familiar stone-wash effect, which
is achieved by washing the made-up article with enzymes
and pumice stones.

[0007] However, jeans fashion is now demanding articles
which no longer exhibit this wash-down effect or modific-
tions achieved utilizing this effect. On the contrary, the
demand is for articles which turn darker in washing or other
treatment operations rather than lighter. These articles are so
to speak to behave inversely to conventionally dyed denim.

[0008] Prior art ring-dyed denim cannot provide such
effects.

[0009] There is consequently a need for a process for
producing inverse denim that shall be economical in that it
should not require additional cost and an inconvenience on
the part of dyers, but should be simple to carry out, ideally
in dyers’ existing dying equipment.

[0010] The present invention, then, provides such a pro-
cess.

[0011] The present invention relates to a process for
producing cotton warp yarns having an inverse denim effect,
which comprises using an indigo dyeing range to perform
[0012] a dyeing step whereby the cotton warp yarn is
through-dyed with indigo in one pass at a dyeing
temperature of 30 to 90° C. and an indigo concen-
tration of 5-500 g/l and

[0013] a subsequent bleaching step or etching step,
etching here to be understood as meaning a treatment
of a dyed surface wherein the dye is locally
destroyed, as described by M. Peter, H. K. Rouette in
“Grundlagen der Textilveredlung” page 633 et seq.,
whereby the indigo is selectively decolorized on the
surface of the cotton warp yarn. This selective decol-
orization can in principle be carried out oxidatively
or reductively, oxidative decolorization being pre-
ferred.

[0014] The process of the invention thus ideally provides
a colorless product which can be modified to be dark blue by
removing the colorless ring and laying the colored core bare.

[0015] An indigo dyeing range in the realm of the present
invention is a range which consists of one dyeing trough or a
combination of multiple dyeing troughs with squeeze rolls
and subsequent skying sectors (see for example ITB Vered-
lung 2/90, title: Indigo-Färberei: Verfahrens- und maschinen-
technische Lösungen, author: Dipl. Ing. L. Haas).

[0016] Any commercially available indigo may be used.
Indigo is preferably used in amounts of 10-50 g/l and more
preferably in amounts of 20 to 40 g/l.

[0017] It is particularly advantageous to use pre-reduced
indigo to carry out the process of the invention. The pre-
reduced indigo used is ideally produced from indigo without
use of reducing agent, such as sodium dithionite for
example, but by catalytic hydrogenation. It is most advan-
tageous to use indigo in the form of a leuco indigo solution
as described for example in EP 1 097 184 B1 and offered on
the market by DyStar Textilfarben GmbH & Co. Deutsch-
land KG.

[0018] To stabilize leuco indigo, i.e., to back-reduce leuco
indigo which has become oxidized in the dyebath, it is
preferable to use a hydrosulfite excess of 0.1 to 5 g/l and
more preferably 0.2 to 2 g/l. It will be appreciated that in lieu
of the hydrosulfite it is possible to use other suitable reduc-
ing agents, for example glucose or hydroxyacetone, or else
combinations of various reducing agents such as glucose/
hydrosulfite.

[0019] The temperature at which the process of the inven-
tion is carried out is preferably 30-90° C. and more prefer-
bly in the range from 50 to 70° C.

[0020] The process of the invention can be carried out
with or without wetting agent, but preferably it is carried out
in the presence of a wetting agent. Examples of suitable
wetting agents are anionic wetting agents, for example fatty
alcohol ethoxylate, alkanesulfonate, sulfosuccinate, alkyl
phosphate or paraffins and hydrocarbons or else mixtures thereof, and most preference is given to using salts of phosphoric esters. The amounts in which the wetting agents mentioned are used are preferably in the range from 5 to 50 g/l and more preferably in the range from 10 to 25 g/l.

[0021] Dyebath pH in the process of the invention is preferably in the range from 10.5 to 13.5.

[0022] The process of the invention surprisingly lends itself in just one pass to yarns which are through-dyed, i.e., dyed in the core as well in the surface region. The contact time with the dyebath is preferably 8 to 30 seconds and more preferably 15 to 20 seconds. The subsequent skying takes preferably 90 to 130 seconds and more preferably 100 to 110 seconds.

[0023] The dyeing step is followed by a bleaching step wherein the indigo is selectively decolorized on the surface of the cotton yarn, leaving the core of the yarn unchanged.

[0024] Useful bleaching agents include all systems which oxidize indigo, for example hypochlorites, such as sodium hypochlorite or permanganate. But preference is given in particular to permanganate, which exists for example in the form of an alkali metal salt and more preferably in the form of potassium permanganate. Very particular preference is given to a bleaching bath which contains potassium permanganate in an alkaline medium, the potassium permanganate being used in amounts which are preferably from 3 to 100 g/l and more preferably from 20 to 50 g/l.

[0025] The pH is preferably in the range from 8 to 10 and can be set for example with NaOH, for example with 38° Be NaOH.

[0026] It is preferable to adjust the bleaching bath to a viscosity of about 12 to 50 seconds measured using a Ford cup (DIN 53211-4) and more preferably 25 to 45 seconds by means of viscosity moderators. Useful viscosity moderators include for example rheological additives such as polyvinylcaprolactam, polyvinylpyrrolidone and also copolymers thereof, polyetherpolym, associative thickeners, polyurea, polyurethane, sodium alginites, modified galactomannans, polyetherurea, polyurethane, anionic cellulose ethers.

[0027] The bleaching step is carried out at 15 to 90° C. and preferably at room temperature. The contact time with the bleaching bath is preferably 10 to 30 seconds and more preferably 12 to 20 seconds.

[0028] In a preferred embodiment of the process according to the invention, the through-dyeing of the cotton yarn in the dyeing step is followed by rinsing with water, bleaching with permanganate, another rinse and a subsequent treatment with a bisulfite solution and the cycle of bleaching, rinsing and treating with bisulfite is repeated at least once.

[0029] It is particularly advantageous for there to be four to six cycles of bleaching, rinsing and treating with bisulfite.

[0030] An intervening drying between dyeing step and bleaching can be used to further enhance the rinsing effect achieved by the bleaching.

[0031] The rinsing between bleaching bath and bisulfite bath can be carried out in 1 to 3 passes and be associated with a skying of 0 to 120 seconds.

[0032] The bisulfite bath preferably contains 10 to 100 g/l and more preferably 20 to 50 g/l of bisulfite. The bisulfite bath can likewise be followed by a skying of 0 to 120 seconds.

[0033] It is a particular advantage to dyers that the dyeing step of the process according to the invention is complete after just one pass. This is because this leaves dyers with the option of using the other dyeing troughs of the indigo dyeing range which are not needed for dyeing to carry out the subsequent bleaching step with or without rinsing and with or without bisulfite treatment. Thus, the equipment needs to be modified only minimally, if at all.

[0034] The cotton warp yarns dyed by the process of the invention can be subjected to further treatment steps to obtain certain effects and then be conventionally woven up and processed into textile articles for the consumer, such as garments in particular.

[0035] However, it is also possible for the dyed and surface-bleached cotton warp yarns to be processed into textile articles without further treatment and, if desired, only to undertake further treatment steps, i.e., to modify the already made-up merchandise. It is of course similarly possible to subject not only the dyed and bleached cotton warp yarns but also the textile articles produced therefrom to further treatment steps.

[0036] The cotton warp yarns dyed by the process of the invention can of course also be woven up, and further processed into articles for the consumer, in admixture with further materials. Blends with elastane may be mentioned by way of example.

[0037] The inverse denim effect of the cotton warp yarns dyed and bleached according to the invention can be made visible, for example, by removing the undyed outer ring of the yarn through washing or some other mechanical stressor and the dark-dyed core coming to light as a result.

[0038] In a further implementation of the process according to the invention, the cotton warp yarn surface decolorized in the bleaching step is stabilized in a third step. Thus, the inverse denim effect can be reinforced by treating the surface with for example TiO₂ in the presence of binders, such as acrylate copolymer or polyurethane. In the same way, the surface can be modified not just to be white but also to be colored, for example with colored pigments, such as vat dyes in pigment form, or else disperse dyes.

[0039] It is of course also possible for the third step mentioned not to be carried out until after the cotton warp yarn has been woven up, for example on the final made-up textile product.

[0040] The present invention also provides textile articles comprising cotton warp yarns dyed by the process of the invention. Examples of such textile articles are denim fabrics which have not been made up, but in particular garments such as pants, skirts, shirts, jackets, etc. or other textile type articles.

[0041] The examples which follow illustrate the invention. The parts in the table examples are by weight.

**EXAMPLE 1**

A) Dyeing Step

- **[0042]** A commercially available unpertreated dry cotton warp yarn was dyed from a dyeing liquor of the following composition:

  - **[0044]** 20 g/l of indigo as commercially available Dye-star Indigo Vat 40% solution
  - **[0045]** 2 g/l of hydrosulfite (BASF Hydrosulfit konz.)
20 g/l of wetting agent (Primasol NF)

The pH of the liquor was 13.

The yarn was dyed at 50° C. in the course of a dip time of 25 seconds. The subsequent skying took 120 seconds.

This was followed by two rinses with water at 20° C.

A through-dyed yarn having a high level of applied indigo was obtained. A dye analysis of the dyed yarn revealed a level of 5.8%.

B) Bleaching Step

The dyed yarn obtained as per A) was dyed with potassium permanganate (20 g/l) at a temperature of 25° C. and a pH of 8.5. The contact time with the bleaching bath was 18 seconds.

The yarn was then led directly into a bath of 30 g/l of hydrosulfite (pH: 8.5, temperature: 25° C.) and subsequently rinsed at 20° C. The cycle of bleaching, treating with hydrosulfite and rinsing was subsequently repeated twice.

EXAMPLE 2

A yarn dyed as per step A) of example 1 was treated at a temperature of 25° C. with a bath containing

200 g/l of thickener (Monagum, 10%)
150 g/l of etching agent (Magnatrop W),
80 g/l of moisture donor (Ätzverstärler HN),
10 g/l of aqueous sodium hydroxide solution and
150 g/l of Rongalit C

for 17 seconds, intermittently dried and steamed at 102° C. for 1 minute. This was followed by washing off at 60° C. and then at 20° C.

EXAMPLE 3

Dyeing Example at Size Application

A yarn treated as per steps A) and B) of example 1 was intermittently dried on a contact dryer and then treated at a temperature of 30° C. with a size bath containing

200 g/l of binder (Perapret PU),
30 g/l of thickener (Primasol AMK),
100 g/l of white pigment (Acramin Weiß DRN 01),
and subsequently set on a contact dryer.

EXAMPLE 4

Dyeing Example at Size Application

A yarn treated as per steps A) and B) of example 1 was intermittently dried on a contact dryer and then treated at a temperature of 30° C. with a size bath containing

200 g/l of starch ether
350 g/l of titanium dioxide
300 g/l of binder (Perapret PU)
100 g/l of Imperon Orange K-G (C.I. Pigment Yellow 5)
and subsequently set on a contact dryer.

EXAMPLE 5

Dyeing Example at Size Application

A yarn treated as per steps A) and B) of example 1 was intermittently dried on a contact dryer and then treated at a temperature of 30° C. with a size bath containing

200 g/l of starch ether
300 g/l of binder (Perapret PU)
50 g/l of Indanthren Gelb 5° GF-D (C.I. Vat Yellow 46)
and subsequently set on a contact dryer.

EXAMPLE 6

Dyeing Example at Size Application

A yarn treated as per steps A) and B) of example 1 was intermittently dried on a contact dryer and then treated at a temperature of 30° C. with a size bath containing

200 g/l of starch ether
400 g/l of titanium dioxide
300 g/l of binder (Perapret PU)
150 g/l of Dianix Gelb P6G fl. (C.I. Disperse Yellow 114)
and subsequently set on a contact dryer.

The table examples which follow describe further embodiments of the process of the invention. They are carried out similarly to the abovementioned examples 1 to 3.

<table>
<thead>
<tr>
<th>Product</th>
<th>Bleaching example</th>
<th>Aftertreatment example</th>
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</thead>
<tbody>
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<td>4</td>
<td>5</td>
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<tr>
<td>Potassium permanganate</td>
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<td>50</td>
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<tr>
<td>Sodium hypochlorite</td>
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<td>10</td>
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<tr>
<td>Sodium persulfate</td>
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<td>10</td>
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<tr>
<td>Inorganic salt</td>
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<td></td>
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<tr>
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<tr>
<td>Reducing agent</td>
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<td>30</td>
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<tr>
<td>Sodium bisulfite</td>
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<th>Bleaching example</th>
<th>Aftertreatment example</th>
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<td>4 5 6 7 8 9 10 11 12 13</td>
<td>14 15 16 17 18 19 20</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>100 400 350</td>
<td></td>
</tr>
<tr>
<td>Polyurethane</td>
<td>200 300 300</td>
<td></td>
</tr>
<tr>
<td>Colored pigment*</td>
<td></td>
<td>100 200</td>
</tr>
<tr>
<td>Temperature (°C)</td>
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<td>40 40 40 30 30 30</td>
</tr>
<tr>
<td>pH</td>
<td>11.2 12 11 10.6 6.5 6.5 6.5 8.5 8 8</td>
<td>6.5 6.5 8 8 8</td>
</tr>
</tbody>
</table>

*colored pigment here refers not only to pigment dyes but also to vat dyes, which are present in their oxidized form, as a pigment, but also disperse dyes.

1. A process for producing cotton warp yarns having an inverse denim effect, which comprises using an indigo dyeing range to perform a dyeing step whereby the cotton warp yarn is through-dyed with indigo in one pass at a dyeing temperature of 30 to 90° C. and an indigo concentration of 5-500 g/l and a subsequent bleaching step whereby the indigo is selectively decolorized on the surface of the cotton warp yarn.

2. A process according to claim 1 that utilizes indigo in the form of a solution of leuco indigo.

3. A process according to claim 2, wherein the leuco indigo has been produced from indigo by catalytic hydrogenation.

4. A process according to claim 1 wherein the process is further carried out in the presence of a wetting agent.

5. A process according to claim 4, wherein the wetting agent is used in amounts of 5 to 50 g/l.

6. A process according to claim 1, wherein the bleaching step is effected by means of a bleaching bath which contains potassium permanganate as bleaching agent.

7. A process according to claim 1, wherein the bleaching step is effected by means of a bleaching bath which contains a thickener.

8. A process according to claim 1, wherein the through-dyeing of the cotton warp yarn in the dyeing step is followed by rinsing with water, bleaching with permanganate, another rinse and a subsequent treatment with a bisulfite solution and the cycle of bleaching, rinsing and treating with bisulfite is repeated at least once.

9. A process according to claim 1, wherein the bleaching step is followed by a third step whereby the cotton warp yarn surface decolorized in the bleaching step is treated with a pigment suitable for cotton.

10. A textile article comprising cotton warp yarns dyed by a process according to claim 1.

11. A process according to claim 3, wherein the process is further carried out in the presence of a wetting agent.

12. A process according to claim 11, wherein the wetting agent is used in amounts of 10 to 25 g/l.

13. A process according to claim 1, wherein said indigo concentration is 10-50 g/l.

14. A process according to claim 1, wherein said indigo is a pre-reduced indigo.

15. A process according to claim 14, wherein the pre-reduced indigo is produced from an indigo without the use of a reducing agent.

16. A process according to claim 2, wherein the temperature is from 50 to 70° C.

17. A process according to claim 1, wherein the dyeing is conducted at a pH from 10.5 to 13.5.

18. A process according to claim 12, wherein the wetting agent is fatty alcohol ethoxylate, alkane sulfonate, sulfon-succinate, alkyl phosphate, paraffin, hydrocarbon or mixtures thereof.

19. A process according to claim 12, wherein the wetting agent is a salt of phosphoric esters.

20. A process according to claim 6, wherein said potassium permanganate is used in an amount from 20 to 50 g/l.

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