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(54) **Printing process on textile products made of cotton, other natural cellulosic fibers and mixed thereof, and textile products thus obtained**

(57) The process according to the invention consists in applying a printing paste containing high concentrations of strong alkali and moisture conditioning agents on a substrate in cotton or other natural cellulosic fibers and mixed thereof. The paste is applied through a printing matrix on which there is formed a certain pattern, and the substrate immediately undergoes a drying step at medium-low temperature and a steaming step, whereby the printing pattern becomes reproduced on the textile substrate by mercerized areas (due to the strong alkali) and non mercerized areas separated by well defined and clear borders.

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Description

[0001] The present invention concerns the field of textile production. More specifically, it concerns a new process for obtaining new and peculiar surface designs through printing on textile products (fabrics or garments) made of cotton or other natural cellulosic fibers, pure or mixed.

[0002] Textile printing, in general terms, consists of applying printing pastes - containing dyes or pigments - to textile products. This step is followed by one or more stabilization steps, comprising physical and/or chemical treatments having the purpose of stably and locally fixing the dying substances. A more precise, though brief, consideration of the various kinds of known printing systems, can be found in the introductory part of the description of European Patent Publication n. EP1591582, in the name of the same applicant, herein incorporated for reference.

[0003] As far as the fabrics made of cotton or other natural cellulosic fibers (or mixed thereof) are concerned, the most widely used printing processes are the direct or application printing (using colored pigments or dying substances belonging to various categories of dyes such as direct or substantive dyes, reactive dyes or reduction dyes), the corrosion printing, the resist printing and the thermal transfer printing. In this latter system, contrary to the more traditional technologies, the printing is not carried out directly on the textile support, but in two steps, firstly printing a support having a perfectly plane and stable surface (release paper) with appropriate colorants, and subsequently transferring the design on the fabric with processes making use of dry heat (sublimation, thermoplasticity), or wet heat (migration, steaming).

[0004] It is also known the phenomenon of the so-called "mercerization" of the cotton-type textile product, when undergoing the action of highly concentrated solutions of sodium hydroxide and, more generally speaking, alkaline solutions. Solutions of concentrated alkali (e.g. sodium hydroxide in a concentration between 150 and 300 g/l), cause structural modifications in the organization of the cellulose macromolecules which constitute the cotton fibers. These modifications bring about, as the most evident effect, a swelling of the fiber, which take on a rounder appearance, and a consequent shortening, with increase of elasticity, dye affinity and lustre.

[0005] In the finishing of textile materials, two kind of mercerizing treatments are normally used: the tension mercerization and the slack mercerization. The tension mercerization consists in treating cotton twisted yarns or fabrics with concentrated alkali, in particular conditions of mechanical tension, in order to confer to the products the characteristics already, in part, mentioned: increase of the dye affinity and effectiveness, of the lustre and brightness, improvement in the mechanical properties, modification of the "feel" of the fabrics and increase of elasticity, better dye coverage of dead and/or immature cotton, increase in the dimensional stability of the fabrics when undergoing the maintenance cycles (e.g. the washing cycles). The slack mercerization treatments, generally applied to fabrics, enhance the elastic behavior of the same, and their dye affinity, without however significantly increasing the lustre.

[0006] The mercerization is sometimes exploited in the printing operations on cotton materials, by using printing pastes containing high concentrations of strong alkali, namely sodium hydroxide, or applying to the textile substrate a strongly alkaline concentrated solution, after that the same substrate has been printed with a resin for resisting to the effect of the alkali. In both cases, in a subsequent resting step (known as "relax" step) the printed material is kept at rest for a time variable between 5 and 15 minutes, so that a mercerization effect develops, localized in the areas selectively interested by the alkaline attack (the printed areas in the first case, the non printed ones in the second).

[0007] In this way one obtains peculiar effects due to the structural localized variations caused by the chemical process of mercerization, applied in certain areas determined by the printing design or pattern. In particular, the cotton fibers in the areas come into contact with the concentrated alkali of the printing paste, modify their morphological structure, increasing the dye affinity and varying their physical and mechanical properties, e. g. significantly increasing the elasticity. As a result, the fabric becomes shrunk in the mercerized areas, with consequent undulations in the non treated areas.

[0008] The above mentioned technique, in both variants, has however two kinds of drawbacks. Firstly, the resting step involves a significant slowing down of the production speed. Secondly, the mercerization in the resting step creates a final pattern, defined by the mercerized areas, which is not neatly defined, and does not correspond to the one originarily set by the printing matrix. In fact, during the rest time, there occurs a migration, significant and controlled to a various extent, of the alkaline solution from the regions of the fabric on which it was applied through the printing step. This migration is due to the hydrophilic properties of the cotton fibers, which unavoidably show up in presence of an aqueous solution of concentrated alkali in a cotton fabric. The variation of the moisture level, and above all of the pH of the adjacent printed areas can then cause an hydrolytic action of the bond between the colorant substance and the fibers, with consequent migrations of the colorant substances towards the areas with the higher moisture content (areas which where subject to the mercerization). Moreover, when the fabric is folded at rest, in case of a simultaneous traditional printing with reactive or direct dyes or pigments, undesired blots of color may derive from the contact between the various folds. The aesthetical attractiveness of this productive solution is then seriously spoiled, and there is also a poor reliability and repeatability of the result.

[0009] The applicant has now surprisingly identified a new process that, improving the aforementioned printing techniques, allows to obtain on the textile material, with shorter productive times, effects of selective, designed mercerization in which the mercerized area have neat and well defined borders, corresponding in a reliable and repeatable way to

those set by the printing pattern, so as to attain new aesthetical results, with effects of designed localized creasing (crepon effect) having an outstanding clarity.

[0010] Such a result is achieved, according to the present invention, with a printing process that can be used on a textile substrate in cotton or other natural cellulosic fibers and mixed thereof, the essential features of which are defined in the first of the appended claims.

[0011] In practice, the process according to the invention consists in applying, on products made of cotton or other natural cellulosic products and mixed thereof (in a raw condition or bated without alkali) of printing pastes containing, above and beyond appropriate thickening, wetting and anti-foam agents and a high concentration of strong alkali, moisture conditioning agents (e.g. polyalcohols in general, namely glycerin) for maintaining in the printed areas a moisture level which is sufficient for a mercerization effect to develop.

[0012] The process comprises a first further step in which the printed textile material is dried at a medium-low temperature. The drying prevents that the mercerization can start, thus avoiding the migration of the strong alkali from the printed areas to the adjacent ones. However, in the printed areas, due to the presence of the strong alkali and of the moisture conditioning agents, a certain moisture level; thanks to this, after the drying step and with suitable heating, via a steaming treatment, an actual mercerizing effect can progress and be fixed. Finally, the textile material undergoes washing (rope or open wide washing) and neutralization steps.

[0013] It is indeed thanks to the fact that the mercerization develops in the steaming step, after the drying has precisely fixed the design in the original configuration set by the print, that the mercerized and non mercerized areas become separated by clear and well defined borders, precisely corresponding to those of the design pattern to be printed. The aesthetical accomplishments of this type of productive solution can then be really and fully exploited, obtaining new results, with crepon design effects having outstanding and neatness and clearness. Moreover, the absence of the resting step, no longer necessary, makes the process faster and simpler, also from the point of view of the logistics and of the productive cost.

[0014] The printing paste having mercerizing properties can be neutral or colored, but with dyeing substances resisting to strongly alkaline conditions. In the second case, it is possible to realize, in a single printing run, also a dye of the product in the mercerized areas. The dye can also be carried out in the part of the design pattern not interested by the mercerization, obtaining different colors in the various printing cylinders/screens that are used.

[0015] The features and advantages of the printing process on textile products made of cotton, or other natural cellulosic fibers and mixed thereof for obtaining designs defined by areas having different mercerization characteristics, and of the products so obtained will be apparent from the following description of an embodiment thereof, given purely as a non-limiting example.

[0016] According to the invention, the process can be applied on textile substrates consisting of woven or knitted fabrics or of manufactured garments, made of raw cotton (pure cotton or mixed with high percentage of raw cotton and fibers resisting to strong alkaline conditions). Said products can even be previously printed fabrics or garments.

[0017] The sequence of the processing steps can be considered, *per se,* analogous to a conventional printing process. Therefore, first of all there is a preparation step of the printing paste containing the strong alkali, the moisture conditioning agents and the other auxiliary components normally present in the traditional printing pastes. As mentioned, the printing paste can also contain dyeing substances, if resistant to the strong alkali.

[0018] The paste can then be applied with any known method (screen printing - with manual, semi-automatic or automatic systems -, hollow cylinder rotary printing, cylinder or roller printing), with a speed that may vary as a function of the technique that is used and the desired results. Also the penetration of the printing paste can be adjusted as a function of the effect one wishes to obtain. The pattern of the printing matrix, and consequently the design that will be defined on the fabric by the areas with different mercerization characteristics, can be of any kind, that is, geometrical, flowery, generally fancy.

[0019] Immediately after the printing step, which may also comprise traditional printing runs for dying the product, a drying step will follow with hot air drying machines, at medium-low temperature (comprised between about 60°C and 120°C), for the time required for the various printing pastes to dry, reaching such a thickness to stably fix on the fabric (maintaining however a certain moisture level due to the presence of the conditioning agents). The time will vary depending on the kind of fabric and also of the type of machines one has available.

[0020] A steaming step follows, on traditional apparatus known to the skilled person, with process conditions that, as an example, may provide for the use of saturated steam at a temperature comprised between about 95°C and 105°C, for a time of about 10÷15 minutes. As mentioned, at this stage the real mercerization develops and is fixed on the textile substrate, due to the presence of the strong alkali and of the moistening agents in the printing paste, kept stable in the desired regions thanks to preliminary dry, while the moisture conditions are maintained suitable for an appropriate advancement of the reaction.

[0021] A final washing and neutralizing step will have the aim of washing away the residuals of strong alkali of the printing paste. In case a simultaneous dying has been carried out in the printing step, the washing will also be useful for getting away with the unfixed dyeing substances and/or pigments. The washing can be carried put with continuous or

discontinuous processes, depending on the devices one has available. The temperature and other washing conditions are set as a function of the type of printed textile material and of the device in use. All the above mentioned steps are obviously carried out with apparatus fully known of to the person skilled in the art.

[0022] Turning back to the core of the process, that is to the say to the printing step, a preferred preparation of a printing paste with strong alkali is expressed by the following recipe.

Chronological order	Products	Amount (/kg of paste)
1	**Purified water**	**as needed**
2	**Strong alkali** (e.g. sodium hydroxide - aqueous solution 32%)	**500 ÷ 850 g**
3	**Wetting agent** (e.g. sodium alkane sulfonates with alkyldiols) INVADINE MR®(Ciba Specialty Chemicals S.p.A.)	**10 ÷ 15 g**
4	**Moisture conditioning agent** (e.g. glycerine)	**30 ÷ 50 g**

[0023] The use of the wetting agent ensures a correct and homogeneous penetration of the printing paste in the textile substrate. The composition thus obtained is slowly agitated and then is added to with a thickening agent, according to the following specifications, so that the paste acquires the suitable thickness in view of the subsequent use.

Chronological order	products	Amount (/kg of paste)
5	**Thickening agent** (e.g. dispersion of acrylic copolymers in light mineral oil) - ALCOLPRINT DT-CS® (Ciba Specialty Chemicals S.p.A.)	**35 ÷ 65 g**

[0024] The mixture is then quickly agitated until the desired viscosity is obtained.

[0025] In case of a paste with dying properties, am exemplifying recipe can be as follows.

Chronological order	Products	Amount (/kg of paste)
1	**Purified water**	**as needed**
2	**Strong alkali** (e.g. sodium hydroxide - aqueous solution 32%)	**700 ÷ 850 g**
3	**Wetting agent** (e.g. sodium alkane sulfonates with alkyldiols) INVADINE MR®(Ciba Specialty Chemicals S.p.A.)	**10 ÷ 15 g**
4	**Moisture conditioning agent** (e.g. glycerin)	**100 ÷ 150 g**

[0026] The composition thus obtained is slowly agitated and then is added to with a thickening agent, so that the paste acquires the suitable thickness in view of the subsequent use. Dyeing substances and relative auxiliary components are also added, according to the following specifications.

Chronological order	Products	Amount (/kg of paste)
5	**Thickening agent** (e.g. starch)	**20 ÷ 40 g**
6	**Dyes** (e.g. reduction dyes [Indantrene®]) **Pigments**	e.g. **50 g**
7	**Reducing agent** (e.g. RONGALITE® C (BASF AG)	e.g. **100 g**

[0027] The mixture is then quickly agitated until the desired viscosity is obtained. The preparation of the paste will be carried out with the mixing and agitation techniques usual in the field of the textile printing.

[0028] Variants and/or modifications can be brought to the printing process on textile products made of cotton or other natural cellulosic fibers and mixed thereof for obtaining surface designs defined by areas having different mercerization characteristics, and to the textile products thus obtained according to the present invention, without for this reason departing from the scope of protection of the invention itself as defined by the appended claims.

Claims

1. A process to be used on a textile substrate comprising cotton or other natural cellulosic fibers, the process comprising a printing step in which a printing paste is directly applied on said substrate by means of a printing matrix on which there is formed a pattern to be reproduced, said printing paste comprising a high concentration of strong alkali for defining on said substrate areas with different morphological structure, in accordance with said pattern of said matrix, as a result of a mercerization reaction triggered on said fibers by said strong alkali, the process being **characterized in that** it further comprises, immediately after said printing step, a drying step at a medium-low temperature and a steaming step, and by the fact that said printing paste further comprises moisture conditioning agents for maintaining in the printed areas, during said drying step, a moisture level which is sufficient for the actual mercerization effect to develop and be stably fixed on said substrate during said steaming step.

2. The process according to claim 1, wherein said moisture conditioning agents consist of polyalcohols.

3. The process according to claim 2, wherein said moisture conditioning agents comprise glycerine in a concentration comprised between about 30 and 50 g for each kg of printing paste.

4. The process according to any of the previous claims, wherein said strong alkali comprise sodium hydroxide in aqueous solution 32%, about 500 ÷ 850 g of said solution being used for obtaining each kg of printing paste.

5. The process according to claim 2, wherein said printing paste further comprises dyeing substances resistant to strongly alkaline conditions.

6. The process according to claim 5, wherein said moisture conditioning agents comprise glycerine in a concentration comprised between about 100 and 150 g for each kg of printing paste.

7. The process according to claim 5 or 6, wherein said strong alkali comprise sodium hydroxide in aqueous solution 32%, about 700 ÷ 850 g of said solution being used for obtaining each kg of printing paste.

8. The process according to any of the previous claims, wherein said printing paste further comprises a thickening agent.

9. The process according to claim 8, wherein said thickening agent is a synthetic agent, used in a concentration comprised between about 35 and 65 g for obtaining each kg of printing paste.

10. The process according to claim 8, wherein said thickening agent is a natural agent, used in a concentration comprised between about 20 and 40 g for obtaining each kg of printing paste.

11. The process according to any of the previous claims, wherein said printing paste further comprises wetting substances.

12. The process according to any of the previous claims, wherein said drying step is carried out at high temperature, comprised between about 60° and 120°C.

13. The process according to any of the claims 1 to 6, wherein said steaming step provides for the use of saturated steam at a temperature comprised between about 95°C and 105°C, for a time of about 10÷15 minutes.

14. The process according to any of the previous claims, wherein said textile substrate undergoes a final washing or neutralization step in order to eliminate the residuals of strong alkali in the printing paste and possible residual dyeing substances.

15. The process according to any of the previous claims, wherein simultaneously to said printing step, one or more traditional printing runs are carried out for coloring the substrate by applying dying substances or pigments.

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EUROPEAN SEARCH REPORT

Application Number
EP 07 11 6695

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	DE 10 86 209 B (BASF AG) 4 August 1960 (1960-08-04) * column 1, line 1 - column 2, line 28 * * column 3, line 10 - line 41; examples 1,3,4 * -----	1-15	INV. D06M11/40 D06M23/16 D06P1/673 D06P5/00 D06Q1/00
X	DE 32 35 348 A1 (HOECHST AG [DE]) 29 March 1984 (1984-03-29) * page 12, line 33 - page 11, line 21 * -----	1	D06Q1/02

TECHNICAL FIELDS SEARCHED (IPC)

D06M
D06P
D06Q

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	21 December 2007	KOEGLER-HOFFMANN, S

CATEGORY OF CITED DOCUMENTS

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 07 11 6695

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21-12-2007

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- EP 1591582 A **[0002]**