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(72) Inventor: **Paolo, Lenzi**
59100, Prato (IT)

(74) Representative: **Bardini, Marco Luigi et al**
c/o Società Italiana Brevetti S.p.A.
Corso dei Tintori, 25
50122 Firenze (IT)

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(71) Applicant: **Stamperia Altair S.r.l.**
59100 Prato (IT)

(54) **Printing process on raw textile materials, and textile products thus obtained**

(57) In a printing process that can be used on a raw textile substrate in natural and/or artificial cellulose fibers, alone or in combination with raw and/or dyed yarns of different composition, a printing paste is directly applied on the substrate, through a printing matrix carrying the pattern to be reproduced, the printing paste comprising a highly concentrated oxidative agent in a highly

alkaline environment, together with stabilizing agents and complexing agents suitable for making the action of the oxidative agent gradual and for preventing catalytic reactions being triggered that could lead to the fibers being damaged.

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Description

[0001] The present invention concerns the field of textile production. More specifically, it concerns a new process for obtaining surface designs through printing on raw textile materials.

[0002] Textile printing, in general terms, consists of applying printing pastes - containing dyes or pigments - to manufactured 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 dyeing substances. The textile print can be classified based upon the system of application - i.e. the system with which the dyeing substances are applied - and the processing techniques. As for the classification based upon the system of application, the following fundamental types are to be mentioned:

- a) direct or application printing;
- b) corrosion printing;
- c) resist printing;
- d) special prints (transfer or thermal transfer printing, Vigoureux printing, dévoré printing, flock printing, relief printing, printing with foil-coverage effects).

[0003] Based upon the processing techniques, the following division can then be made: screen printing (with manual, semi-automatic or automatic systems), hollow cylinder (rotary) printing, cylinder or roller printing.

[0004] All of the aforementioned treatments are well known to the average man skilled in the art, and will not be described in detail. However, in order to place the present description in the proper context, it is useful to sum up the characteristics of the three main systems of application.

[0005] Direct or application printing is the simplest process. It consists of a direct reproduction of patterns, in one or more colors, on white or lightly colored fabrics. A characteristic of application printing is the reproduction of the pattern on just one side of the textile product. In general, the processing sequence comprises the following steps: I. printing; II. drying; III. fixation/steaming; IV. washing; V. drying. In case of printing with pigments the sequence comprises the first three steps only.

[0006] Corrosion printing is carried out on fabrics dyed beforehand with corrodible dyes, i.e. dyes that can be degraded or discolored by a reducing etching during the steaming step. The corrosion can create a completely white pattern when, in addition to the corroding agent, white pigments (e.g. titanium dioxide) and optical bleaches are used. Very refined and sophisticated pattern motifs, and a rather low print coverage can be obtained. These are the two main reasons that lead to the choice of the corrosion printing process. With this process, effects of "illumination" are obtained with very intricate designs that cannot be made by direct printing.

[0007] Resist printing has the fundamental characteristic of preventing the fixation - in the printed area - of the base dye applied before or after printing. The result is similar to the one obtained by corrosion printing, but resist printing has the advantage of being more cost-effective, when it can replace corrosion. In general, resist printing can be obtained through physical resistance, i.e. application of printing pastes that prevent contact between the fiber and the dye in the subsequent dyeing step (for example batik print), or else chemical resistance, i.e. application of printing pastes containing chemical products that prevent the development of the dye in the printed areas.

[0008] The applicant has now identified a printing process that does not fit into any of the aforementioned known types and that, thanks to novel operating steps, allows a particularly good result to be accomplished in terms of quality and appearance of the textile product obtained, with advantages in terms of simplicity and speed of production, and consequently a favorable impact upon the relative costs.

[0009] Such a result is achieved, according to the present invention, with a printing process that can be used on a raw textile substrate made of natural and/or artificial cellulose fibers, alone or in combination with raw and/or dyed yarns of different composition, the process making use of a printing matrix on which there is formed a pattern to be reproduced, and comprising the step of directly applying on said substrate, by means of the printing matrix, a printing paste comprising a highly concentrated oxidative agent in a highly alkaline environment, along with stabilizing agents and complexing agents for restraining the action of the oxidative agent and for preventing the start of catalytic reactions that could damage the fibers.

[0010] In practice, a localized bleaching according to a certain pattern is carried out through the application of the oxidative agent, namely simple hydrogen peroxide contained in a paste for printing with special characteristics and preparation. The paste is characterized in particular by a very high concentration of hydrogen peroxide and of a strong base (notably sodium hydroxide), a concentration that can vary according to the heaviness and type of raw fabric to be treated, as well as to the degree of whitening that one wishes to obtain, but which is in any case around ten times the maximum normally used in conventional oxidative bleaching processes of cellulose fabrics. The pattern effect is therefore linked to the oxidative degradation of the natural pigments present in the cellulose fibers, caused by the oxidative agent in the aforementioned processing conditions that shall be described in greater detail later on.

[0011] The development of the oxidative action is thus improved during a subsequent drying step with hot air, which preferably takes place in a drying chamber with moderate ventilation at a temperature of between about 65° and 110°C. The drying time can vary between about 1 and 3 minutes and at the end the fabric is left to rest (folded in laps) for about 12 hours.

[0012] The printing paste can be applied, both on fabrics and on manufactured garments, by means of any one of the conventional processing techniques, i.e. with screen printing (with manual, semi-automatic or automatic systems), hollow cylinder (rotary) printing, cylinder printing or roller printing. The result is basically that of a textile substrate having the base color typical of raw manufactured products made of cellulose fibers - i.e. variable from light yellow up to dark grey - in which various types of printed patterns (geometric, flowery, fancy patterns etc.), are formed in lighter color than the base color, with variable penetration effect so that the print is visible only on the front of the fabric or else visible both on the front and on the reverse (two-sided effect) .

[0013] A result in some ways comparable to that obtained according to the invention could be achieved with the methods of the prior art only at the expense of rather long and complex operating steps, and/or in any case unable to ensure an outcome of the same quality. For instance, with a corrosion printing treatment, it would be necessary to preliminarily clean and bleach the raw manufactured textile products, to subsequently dye said products in the characteristic tones of natural cellulose fibers by using corrodible dyes, and finally to carry out the pattern effect with the actual corrosion print, this last step, moreover, being intrinsically lengthy and expensive. As an alternative, by carrying out pigment printing on raw substrates, the printing pattern could be obtained via a direct application of printing pastes with white pigments (e.g. titanium dioxide). In this case, however, the fabric shall have the typical characteristics of materials printed with pigments, first of all a fabric that is remarkably stiffer and harsher, and a print effect that is visible exclusively on the right side of the fabric.

[0014] Other characteristics and advantages of the printing process for obtaining surface designs on raw textile materials, and of the textile products thus obtained according to the present invention shall become clearer from the following description of an embodiment thereof, given purely as a non-limiting example.

[0015] According to the invention, the process can be used on yarns, fabrics and manufactured garments made of yarns of raw linen, raw cotton and whatever other cellulose fiber of natural and artificial origin; or else, it can be used on fabrics and manufactured garments made of raw yarns with a composition 100% of natural and artificial cellulose fibers, along with yarns with a different fiber composition, these being raw and/or dyed. The textile products mentioned above, in order to eradicate any possible traces of heavy metals that may sometimes be present (for example iron salts and/or oxides), are preferably pretreated with the conventional bating and complexation processes normally used in dyeing pretreatment cycles of cellulose textile materials. As an example, the following is a recipe for acid bating treatment.

Acid bating treatment - Discontinuous processing				
Products / conditions	m. u.	Paddle system	Overflow system	Jigger system
Dispersing emulsifying agent (mixture of non-ionic surfactants) INVADINE DA (Ciba Speciality Chemicals S.p.A.)	g/l	1 - 2	1 - 2	-
Dispersing wetting agent (mixture of non-ionic surfactants) ULTRAVON CN (Ciba Speciality Chemicals S.p.A.)	g/l	-	-	2 - 4
Acidifying agent (derived from phosphoric acids with water-soluble polymers) INVATEX SA (Ciba Speciality Chemicals S.p.A.)	g/l	1 - 3	1 - 3	2 - 4
Temperature	°C	40 - 60	40 - 60	40 - 60
Length of treatment	min	30 - 60	30 - 60	45 - 90

Acid bating treatment - Continuous cycle				
Products / conditions	m.u.	Cold storage	Continuous / short time	Continuous / long time
Dispersing wetting agent (mixture of non-ionic surfactants) ULTRAVON CN (Ciba Speciality Chemicals S. p.A.)	g/l	3 - 6	2 - 6	1 - 2
Acidifying agent (derived from phosphoric acids with water-soluble polymers) INVATEX SA (Ciba Speciality Chemicals S. p.A.)	g/l	4 - 8	6 - 12	2 - 4
Impregnation temperature	°C	20 - 40	20 - 60	-
Treatment temperature	°C	environmental temperature	40 - 60	40 - 60
Length of treatment	min	-	0,5 - 2	1 - 3
	hours	2 - 6	-	-

[0016] The sequence of the processing steps can be considered, *per se*, analogous to the conventional direct printing process. Therefore, first of all there is a preparation step of the printing paste, ensuring the oxidative bleaching action according to the invention. A preferred preparation of the paste is expressed by the following recipe.

Chronological order	Products	Amount (/kg)
1	Purified water	as needed
2	Sodium hydroxide (26 Bé [Baumé degrees] solution)	150 - 300 g
3	Sequestering agent for heavy metals (e.g. polyphosphonic acids in aqueous solution) MEPAL FA (Massimo Guarducci s.r.l.)	3 - 5 g
4	Wetting agent (e.g. sodium alkane sulfonates with	10 - 15 g

	alkyldiols) INVADINE MR (Ciba Specialty Chemicals S.p.A.)	
5	5	
10	Stabilizing agent for hydrogen peroxide (e.g. phosphoric derivatives containing ammina- diethylenetriamine pentacetate-dipentasodium) H2O2 STABILIZING AGENT (Massimo Guarducci s.r.l.)	20 - 30 g

[0017] The presence of a complexing agent (sequestering agent) particularly important in case of presence of traces of heavy metals that, catalyzing the decomposition of the hydrogen peroxide, would cause depolymerizations of the cellulose with consequent weakening of the textile structures, up to the point of damaging the textile product as a result of the degradation of the cellulose caused by an unrestrained outburst of the oxidative action. 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)
6	Thickening agent (e.g. dispersion of acrylic copolymers in light mineral oil) - ALCOLPRINT DT-CS (Ciba Specialty Chemicals S.p.A.)	55 - 65 g

[0018] The mixture is then quickly agitated until the desired viscosity is obtained. Finally, the hydrogen peroxide is added, possibly, after a further light agitation, along with the optical bleach, according to the following specifications.

Chronological order	products	Amount (/kg)
7	Hydrogen peroxide (35%)	150 - 300 g
8	Optical bleach (if required) (e.g. derivative of stilbendisulfonic acid) UVITEX BHT liquid or UVITEX CF liquid (Ciba Specialty Chemicals S.p.A.)	2 - 5 g

[0019] Then there follows the step of application of the printing paste on the textile fiber, an application that can take place, as stated, according to any one of the techniques already known, and therefore on conventional apparatuses. The printing speed shall vary, according to what can easily be optimized by an expert operator, according to the technique used and the results required. The penetration extent of the printing paste can also be adjusted according to the

desired effect.

[0020] In the subsequent drying step, carried out as mentioned above, there develops the oxidative effect of the hydrogen peroxide, with the consequent localized degrading of the natural pigments and the formation of the print pattern. A steaming treatment can then take place; the steaming is not essential to obtain the desired print effect but can in any case be used to further develop the oxidative degradation effect. Such a treatment, if carried out in discontinuous apparatuses, can last 10÷20 minutes with saturated steam at a temperature of about 105°C. A final washing step with detergents has the purpose of eliminating the water-soluble oxidative demolition products and the residues of the printing paste. The washing can be carried out equivalently with discontinuous or continuous processes according to the apparatuses available. The washing temperatures and the other conditions are established, based upon common experience, according to the type of textile material and the type of apparatus used.

[0021] According to the invention, a printing process is thus disclosed that is able to achieve substantially new functional and aesthetic results, at least in relation to production methods of comparable simplicity and cost. As already stressed, the specifications of the example just described, although they should be considered advantageous in order to obtain an optimal result, must not be considered as a limitation.

[0022] In fact, variants and/or modifications can be brought to the printing process for obtaining surface designs on raw textile materials, 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 printing process to be used on a raw textile substrate made of natural and/or artificial cellulose fibers, alone or in combination with raw and/or dyed yarns of different composition, the process making use of a printing matrix on which there is formed a pattern to be reproduced, and being **characterized by** the fact of comprising the step of directly applying on said substrate, by means of said printing matrix, a printing paste comprising a highly concentrated oxidative agent in a highly alkaline environment, along with stabilizing agents and complexing agents for restraining the action of the oxidative agent and for preventing the start of catalytic reactions that could damage the fibers.
2. The process according to claim 1, wherein said oxidative agent is hydrogen peroxide, the alkalinity of said paste being controlled by means of a strong base, said oxidative agent and said strong base having, respectively, a concentration of between about 150 and 300 g per kg of printing paste.
3. The process according to claim 2, wherein said strong base is sodium hydroxide.
4. The process according to claim 2 or 3, wherein said stabilizing and complexing agents comprise a stabilizing agent for hydrogen peroxide and a sequestering agent for heavy metals, in a concentration, respectively, between 20 and 30 g per kg of printing paste, and between 3 and 5 g per kg of printing paste.
5. The process according to any one of the previous claims, wherein said paste also comprises a wetting agent in a concentration of between about 10 and 15 g per kg of paste.
6. The process according to any of the previous claims, wherein said paste also comprises an optical bleach in a concentration of between about 2 and 5 g per kg of printing paste.
7. The process according to any of the previous claims, wherein said paste also comprises a thickening agent in a concentration of between about 55 and 65 g per kg of paste.
8. The process according to any of the previous claims, wherein after the application of said printing paste said textile substrate is dried with hot air in a drying chamber with moderate ventilation at a temperature of between about 65° and 110°C, for a time variable between about 1 and 3 minutes.
9. The process according to claim 8, wherein after said drying step said textile substrate is left to rest folded in laps for about 12 hours.
10. The process according to claim 8 or 9, wherein after said drying step said textile substrate is subjected to a steaming treatment and to a final washing step with detergents in order to eliminate the water-soluble oxidative demolition products and the residues of the printing paste.

11. The process according to any of the previous claims, wherein prior to the application of said printing paste, in order to eliminate the possible presence of traces of heavy metals, said textile substrate undergoes a bating and complexing pretreatment.

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